Researches on Camphor, Borneol and Their Allied Substances.

By Seiichi YAMADA.

(Received May , 1941.)

(1) Catalytic Reduction and Oxidation of Camphor, Borneol and Their allied Substances. According to the researches by Aloy and Brustier[1] camphor is obtained quantiatively by passing borneol over copper heated to 300°C, and Neave[2] under the reaction condition akin to that of Aloy and others, obtained *d*-camphor from *d*-borneol but camphene from isoborneol. Later, Masumoto[3] observed that catalytic oxidations of borneol into camphor by reduced copper differ according to the manufacturing process of the latter.

A sample of copper (1) was obtained by reducing copper oxide which was gained from copper nitrate and sodium hydroxide. When this copper was used as a catalyser, the yield of camphor from borneol was at its best at 200°C amounting to 80%, while at 300°C the yield decreased to its half. On the other hand when copper (2) obtained by reducing copper oxide which was gained by using ammonium hydroxide instead of sodium hydroxide was used as a catalyser, the yield of camphor hardly reached 10% even under the best condition. Copper (3) was made according to Sabatier's process by reducing copper oxide which was gained by heating copper nitrate. When this catalyser was used, the results were generally satisfactory, the yield of camphor amounting to 75%. Ikeda[4] reports that when isoborneol was passed over reduced copper prepared by Sabatier's process, only dehydration occurred, and at 130°–140°C, 90% of the isoborneol was changed to camphene.

Isoborneol, inspite of its being a secondary alcohol, is promoted to dehydrate under the catalytic reaction of metals, and thus behaves unlike borneol. In order to investigate more closely the behaviour of the two isomers, the writer, just as Masumoto did, used the three kinds of copper and examined its catalytic reaction upon borneol at 400°C. The result showed that copper (1) yielded camphor quantitatively, copper (2) yielded camphor and camphene in the proportion of 80:20, and copper (3) of 87:13. It seems, therefore, that copper (1) promotes only oxidation of borneol, while coppers (2) and (3), not only oxidation but to some extent dehydration. On the other hand, isoborneol under the catalytic reaction of copper (1) at 150°C and also at 300°C yielded camphor as a reaction product in each case, and with copper (2) at 150°C all of the isoborneol was changed to camphene, and at 300°C camphor and camphene were formed in the proportion of 24:76. In short, copper (1) acts against isoborneol as to promote oxidation independent of the reaction tempera-

(1) *Bull, Soc. Chim.*, [4] **9** (1911), 733.
(2) *J. Chem. Soc.*, **101**, 513.
(3) *Memoirs Coll. Sci. Kyoto Imp. Univ.* **A. 9** (1925), 219.
(4) *Bull. Institute Phys. Chem. Research*, **4** (1925), 343.

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ture, while copper (2) promotes dehydration at low temperatures, but oxidation as the temperature is raised. Therefore, for the purpose of synthesising camphor from bornel and isoborneol copper (1) seems to be the most appropriate catalyser.

The fact that nickel as a catlyser plays as analogous role as copper does has often been pointed out, and according to two patents[5] regarding the action of reduced nickel towad borneol and isoborneol, reduced nickel is almost or completely defectiveof the power to promote oxidation, but when small quantity of either austic soda, sodium nitrate or sodium sulphate is added, the oxidation is very strongly promoted. The writer examined the catalytic action of reduced nickel toward borneol and isoborneol and found that though oxidaion is promoted, there is some difference in the reaction conditions compared with those in the case of reduced copper.

With respect to the catalytic reduction from camphor to borneol and isoborneol, Komatsu and Masumto[6] obtained isocamphane besides small quantity of borneol by reducing camphor in the stream of hydrogen at 180°C under the catalytic reaction of reduced nickel,[7] and Ipatiev,[8] using nickel oxide as a catalyser, tried the reduction in an atmosphere of hydrogen under the pressure of 129 atms. and at 200°C, and obtained borneol and isocamphane. Further, Kubota and Hayashi[9] reported that using reduced copper as a catalyser, camphor was reduced under high pressure of hydrogen and at high temperatures to borneol and isoborneol in the range of proportion from 29:71% to 21:79%. Vavon[10] inferred that by the reduction of camphor isoborneol is formed at first and then this undergoes a rearrangement to form borneol.

The writer using reduced nickel as a catalyser submitted camphor to the catalytic reduction with hydrogen at high temperature and high pressure and found that at about 180°C the proportions of borneol and isoborneol formed were 51:49, 51:50, 47:53 when the pressure of hydrogen were 23, 49, 85 atms. respectively; and when the reaction temperatures were 140–160°C, and 170–190°C the proportions of formation of both of the isomers were 51:49 and 47:53 respectively (cf. Fig. 1–5). When the temperature of reaction is raised above 200°C, hydrogen is absorbed more than 1 mole, and it seems that the alcohol formed at first is subsequently dehydrated and reduced successively, and as a matter of fact isocamphane and a small quantity of water were formed as reaction products (cf. Fig. 6–7). This fact can be explained by deciding experimentally the temperatures of dehydration of borneol and isoborneol; the writer's experiment shows that borneol is dehydrated at 220–260°C and isoborneol

(5) Schering, D.R.P., 219043 (1908); cf. D.R.P. 219044 (1908).
„ D.R.P., 211147 (1908); cf. D.R.P. 271157 (1909).
(6) *Mem. Coll. Sci. Kyoto Imp. Univ.*, **5** (1922), 225.
(7) O. Aschan, "Naphth. Therp. Campherarten" p. 152, 1929; D.R.P. 213154 (1907); *Chem. Zentr.*, **1909**, II, 1025.
(8) *J. Russ. Phys. Chem. Soc.*, **38** (1906); *Chem. Zentr.*, **1906**, II, 87; *Ber.*, **45** (1912), 3212.
(9) *Bull. Chem. Soc. Japan*, **1** (1926), 69.
(10) G. Vavon and P. Peignier, *Bull. soc. chim.*, **39** (1926), 924; *Compt. rend.*, **181** (1925) 183; P. Lipp, *Ber.*, **68** (1935), 1029.

at 160–190°C. From this it is to be sen that the dehydration temperature of isoborneol being in close vicinit of the temperature adequate to the reduction of camphor, the reductin is usually accompanied by the dehydration (cf. Fig. 8–10).

In order to investigate how the yeld of catalytic reduction is influenced by the introduction of solvents, cyclohexane as a non-polar substance on the one hand, and absolute alohol, acetic acid and pyridine as polar substances on the other hand, were used, and the proportions of borneol and isoborneol formed were 23:77, 12:88, 37:63, 36:64 respectively (cf. Fig. 11–15). In the above case, the introduction of solvents increased remarkably the yield of isoborneol, but any relation between this increase and the polarity of solvents s barely recognisable. The addition of absolute alcohol raised the yield of isoborneol, and yield of some 90% was gained.

When camphor (I) is reduced with netallic sodium and ethyl alcohol, borneol is formed mainly, and when camphor is catalytically reduced with metallic catalyser and hydrogen in alcohdic solution the main product is isoborneol. Epi-camphor (II), when reduced with metallic sodium and alcohol gives epi-borneol only, and when catalytically reduced with platinum black and hydrogen in acetic acid solution it gives epi-isoborneol.[11] Nor-camphor (III) gives nor-isoborneol when reduced either with metallic sodium and alcohol or with palladium chloride, platinum colloid and hydrogen in alcoholic solution.[12] This may be due to the fact that the molecular construction of nor-camphor difer from those of camphor and epi-camphor, and a mobile hydrogen is linked with the α-carbon adjacent to C=O group. Then as the chemical constitution of dimethylcamphor, (IV) differs from that of nor-camphor, having in the α-position CH_3 substituted for the mobile hydrogen, under the expectation that dimethylcamphor unlike nor-camphor may form a derivative of borneol as the reduction product, the writer synthesised, according to Haller's process,[13] α, α'-dimethylcamphor from camphor and then reduced it with metallic sodium and alcohol. Thus two kinds of alcoholic compounds A and B were gained in the proportion 88:12, as shown in the following table.

As to the stereochemical configuration of the two alcohols formed, just like in the case of borneol and isoborneol, the less easily dehydrated was defined as dimethylborneol and the easily dehydrated as dimethylisoborneol. Now, dimethylcamphor was heated in hydrogen under 60 atms. at 220–230°C in the presence of reduced nickel and it was found that this reduction was much more difficult than that of camphor, the yield of alcohol being only 19% even after about 27 hours. The proportion of dimethylborneol and dimethylisoborneol formed being 85:15, it was almost the same as when the reduction was done with metallic sodium and alcohol (cf. Fig. 16). When the catalytic reduction was done by adding absolute

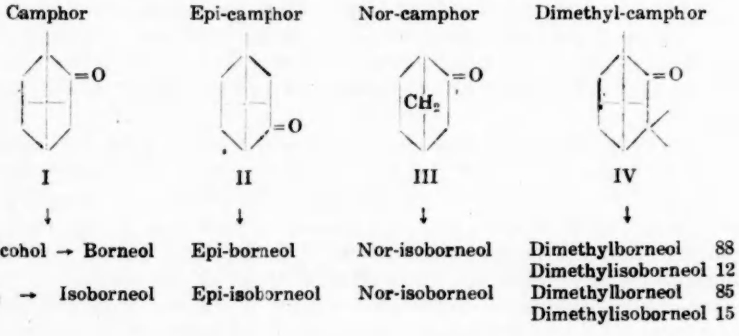
(11) M. Lipp geb. Bredt Savelsbery, E. Bund. *Ber.*, **68** (1935), 249; cf. Bredt and Perkin, *J. prakt. Chem.*, [2] **89** (1914), 254.

(12) Komppa and Beckmann, *Ann.*, **512** (1934), 174; Alder and Stein, *Ann.*, **514** (1934), 220.

(13) *Compt. rend.*, **148** (1909), 1645.

Substance	A	B
B. p.	90.5~93/5 mm	82~83/3 mm
M. p.	57°C	47~49°C
$[\alpha]_D$	+50.72° (in alcohol) at 26° +53.76° (in toluene) at 26°	+36.47° (in alcohol) at 15° +42.71° (in toluene) at 15°
Phenylurethane	112—113°C	116—117°C
p-Nitrobenzoate	Needle crystal of silky luster and of faintly greenish white color. 115—115.8°C	Nearly colourless and lustrous needle crystal. 114.5—115°C
Phthalic acid monoester	Fine, white needle crystal 177—178°C	Lustrous, fine scaly crystal 173—174°C
Magnesium phthalate	Lustrous white scaly crystal 175—176.2°C	Crystalline white powder 180—182°C
Reacting with $ZnCl_2$ or with phthalic anhydride	Not dehydrated	Dehydrated

alcohol or a little acetic acid, the proportions of both of the isomers produced were 66:34 and 86:14 respectively, and the use of absolute alcohol as a solvent increased the yield of iso-compound as in the case of camphor (cf. Fig. 17). When the reduction temperature was raised to 260°–280°C, more than 1 mole hydrogen was absorbed dehydration occurred, and hydrocarbon was formed (cf. Fig. 18).



(2) Isomeric Change between Borneol and Isoborneol. Applying the aforesaid method of separation[14] of borneol and isoborneol to the crude isoborneol (90%), gained by the catalytic reduction of camphor in alcoholic solution, isoborneol which may be considered pure was obtained, and its properties were compared with those of its isomer, borneol.

(14) *J. Chem. Soc. Japan*, **53** (1932), 807.

	M.p.	$[\alpha]_D$	$[\alpha]_D^{15}$
Borneol	204—204.5°C (in a sealed tube)	+3810°C = 3.57 (in alcohol, at 11°)	+38.44°C = 3.92 (in toluene)
Isoborneol	212—213°C (in a sealed tube)	−3442°C = 3.35 (in alcohol, at 7°)	−19.59°C = 5.17 (in toluene)

	Combustion heat	Acetate			
		B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D$
Borneol	Kcal/mol 1489.3	98/11 mm	0.9864	1.4655	+42.75° at 11°
Isoborneol	1472.5	76–77/3 mm	0.9867	1.4623	−51.98° at 18°

	Magnesium phthalate		Methoxy value after etherification with HCl—methyl alcohol
	M.p.	$[\alpha]_D^{15}$	
Borneol	103—104°C	+31.3°C = 1.99 (in alcohol)	0.42
Isoborneol	95—97°C	−29.46°C = 4.0 (in alcohol)	12.5

Borneol and isoborneol being stereoisomers of cis- and trans-form,[15] a transformation from one into the other may be possible as we expect from heats of combustion of the two isomers. And hitherto the transformation of isoborneol into borneol was accomplished by adding alkaline metal to the solution of isoborneol in alcohol, in xylene or in ligroin and then it was heated under pressure;[16] otherwise the solution in cyclohexane was heated to about 200°C in the presence of nickel catalyser with hydrogen under 30 atmos.[17] When isoborneol was heated for about 4 hours in the presence of reduced nickel under 50 atm. hydrogen at 130~150°C and 140~165°C, 16% and 51% of the sample was changed to borneol in each case; conversely it was seen that only 1% of borneol was transformed to isoborneol, when heated for about 20 hours in the presence of reduced nickel under 70 atm. hydrogen at 170~190°C (cf. Fig. 19). Further, when each of the solutions of borneol and isoborneol in absolute alcohol was heated for 20 hours in the presence of reduced nickel under 70 atms. hydrogen at 150~160°C and 130~140°C respectively, 10% of borneol was transformed to isoborneol and 11% of isoborneol to borneol (cf. Fig. 20–21).

(3) Dehydration of Borneol and Its allied Substances. Formerly dehydrating agents used for the dehydration of borneol and isoborneol

(15) Vavon and Peignier, *Bull. soc. chim.*, [4] **39** (1926), 666, 924; Hückel, *Ann.*, **477** (1930), 157.

(16) Wagner and Brickner; *Chem. Zentr.*, **1909**, II, 25; Schmitz & Co., D.R.P., 212, 908; *Chem. Zentr.*, **1909**, II, 1392.

(17) H. Sandkuhl, Rhein. Kampf. Fabr. Düsserdorf—Oberkassel, D.R.P., 408666, *Chem. Zentr.*, **1925**, I, 1809.

were zinc chloride, phosphorus pentoxide, potassium bisulphate, sulphuric acid, oxalic acid, glacial acetic acid, phthalic anhydride and active carbon; and although isoborneol forms easily camphene, the dehydration of borneol is very difficult, and therefore the reaction has been utilized to distinguish these two isomers. But, if an adequate reagent is found, the dehydration of borneol may be executed. Therefore, for the dehydration of borneol and isoborneol the writer used $H_2SO_4.3H_2O$, which Sendrens[18] recommended as a good dehydrating agent for alcohol. When 0.07 mol of $H_2SO_4.3H_2O$ was added to 1 mol of isoborneol and the mixture was heated at 140~145°C for 10 hours, dehydration occurred easily and 56% camphene and 18% ether compound of high boiling point were obtained; borneol, under the same condition, gave 63% camphene and 12% ether.

No.	Substances	Method of preparation	M.p. °C	B.p. °C	d_4	n_D	$[\alpha]_D$
1	Di-*d*-bornyl-ether[19]	Dehydration with $ZnCl_2$	43–44	317/753 mm	—	45°C 1.4810	18°C +65.6°
2	Di-*l*-bornyl-ether[20]	Dehydration with conc. H_2SO_4	liquid	312–314	18°C 0.9600	24°C 1.4940	−88.56°
3	Di-*d*, *l*-isobornylether[21]	Action of conc. H_2SO_4 to camphene	90–91	322	—	—	—
4	Di-*d*-bornyl-ether	Dehydration with $H_2SO_4.3H_2O$	liquid	134–137/2 mm	20°C 0.9564	20°C 1.4927	27°C +41.68°
5	Di-*d*, *l*-isobornylether	,,	,,	134–145/2 mm	20°C 0.9672	20°C 1.5010	—

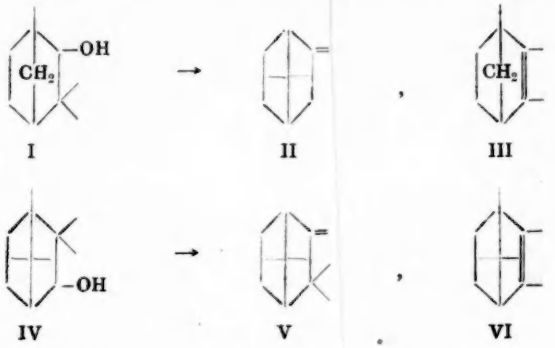
In addition, when dry alumina is acted on borneol at 350°C dehydration occurs and a good yield of racemic camphene is obtained.

By dehydrating borneol $[\alpha]_D$+18.62° and isoborneol $[\alpha]_D$−15.72° with $H_2SO_4 3H_2O$, there were obtained solid camphenes $[\alpha]_D$+3.3° and $[\alpha]_D$+4.35° respectively; and by dehydrating isoborneols $[\alpha]_D$−15.72° and $[\alpha]_D$−34.42 with phthalic anhydride, solid camphenes $[\alpha]_D$+25.25 and +49.33 were obtained respectively. The rotatory powers of camphenes thus formed were seen to be influenced both by the time and temperature of reaction. And, in order to find out the cause of this change in the rotatory power of camphene, active camphene was directly treated with alumina, phthalic anhydride, hydrochloric acid, $H_2SO_4.3H_2O$, 50% H_2SO_4 and acetic acid, and in each case the rotatory power decreased gradually and it was recognised that the velocity of racemisation was affected not only by the time and temperature of reaction but also by the kind, concentration, and quantity of the acid itself. When bornyl acetate was set to reaction of $H_2SO_4.3H_2O$ for 10 hours at 140~145°C, both isomerisation and dehydration occurred and 0.5 mol % isobornyl acetate and 3 mol % camphene were obtained; again when treated under the same conditions, 75 mol % isobornyl acetate

(18) Sendrens, *Compt. rend.*, **154** (1912), 1168; *ibid.*, **177** (1923), 1183.
(19) Tetsusaku Ikeda, *J. Chem. Soc. Japan*, **48** (1927), 491.
(20) Gulbew, *Chem. Zentr.*, **1913**, I, 24.
(21) Bouchardat and Lafont, *Bull. soc. chim.*, [3] **11**, 902.

changed into camphene. Camphene in acetic acid solution changed as much as 50 mol % into isoboryl acetate, when treated under the same conditions.

Some time ago, Toivonen and Tiklanen[22] obtained a mixture of *a*-fenchene (II) and methylsantane (III) by dehydrating fenchyl alcohol (I) with aluminium phosphate. Hence, it is suspected that the hydrocarbons obtained by dehydrating dimethylborneol (IV), which has a chemical constitution similar to that of fenchyl alcohol, may be camphene form (V) and bornylene form (VI), as vill be shown below:



I II III

IV V VI

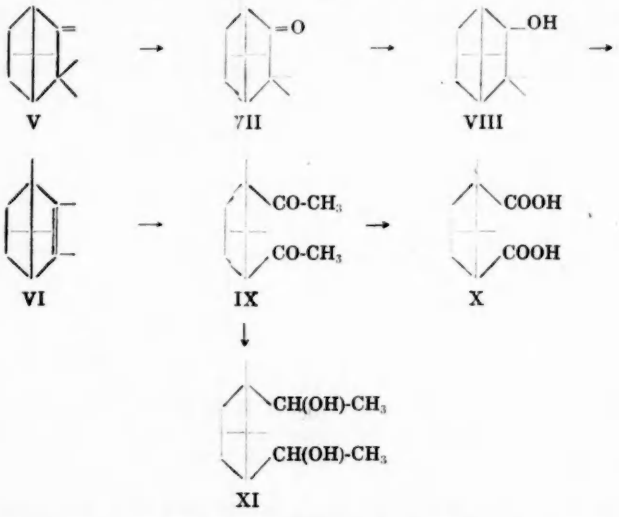
When dimethylborneol was heated with $H_2SO_4.3H_2O$ at 140~145°C for over 10 hours, a mixture of hydrocarbons (B.p. 48~82°/5 mm.) was obtained, the yield being 71%. When dehydrated with phosphorus pentoxide, a single hydrocarbon (VI) (b.p. 192~193°C, d_4^{25} 0,8754, n_D^{25} 1,4765, $[\alpha]_D^{19}$ −5.76°) was obtained; and when dehydrated with phthalic anhydride, a product to be suspected as a mixture of hydrocarbons was obtained, but as the sample was too scanty, further study could not be executed. The hydrocarbons obtained by dehydrating with $H_2SO_4.3H_2O$ were most probably a mixture of two hydrocarbons; but as it was impossible to separate it into its components even after eight fractional distillations, the writer tried anew to separate it in the form of oxidised compound, by submitting its chloroform solution to ozone oxidation. As its result, two compounds were obtained:

Subs.	B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D$	Remarks
A	72–73/6 mm	0.9473	1.4712	+27.06° at 9°C	Colourless
B	120–123/6 mm	1.0087	1.4746	− 6.87°	Yellowish green, viscous, easily decomposes during distillation.

Substance A, as it forms semicarbazone (M.p. 243.6~243.9°C), and gives a product to be considered as alcohol VIII (B.p. 82~86°/5 mm, d_4^{25}

(22) *Chem. Zentr.*, **1931**, II, 2150.

0.9581, n_D^{25} 1,4831, $[\alpha]_D$+1.5) when reduced with metallic sodium and alcohol, might be a monoketone (further confirmation was desirable, but as the sample run short we postponed it to the future.) Substance B was inferred to be a diketone (IX), as it is changed to camphoric acid (X) by the oxidation with nitric acid of sp. gr. 1.29 or by decomposition during distillation, and also as it gives three kinds of what may be considered as glycol isomers (XI) when reduced with metallic sodium and alcohol. The reactions are shown by the following scheme:



In addition, when the mixture of hydrocarbons was oxidised with ozone in a solution of benzene, the following substance of the physical constants, to be considered as a dextro-rotatory diketone, was obtained.

B.p. 112–114°/4mm	d_4^{25} 1.0166	n_D^{25} 1.4749	$[\alpha]_D$ +38.91°

The content of the A- and B-compounds in the product of ozone oxidation was determined to be in the proportion of 43:57. Borneol and isoborneol, when dehydrated, give chiefly camphene alone; while dimethylborneol, a substitution product of methyl radical in place of α-hydrogen, forms hydrocarbons of both camphene and bornylene forms after dehydration.

(4) Hydration of Camphene. Camphene, by the hydration with a mixture of 50% H_2SO_4 and glacial acetic acid, gives in addition to isoborneol about 10% of borneol. Camphene $[\alpha]_D$+72.69°, obtained by the process of A. Reychler,[23] was hydrated with 50% sulphuric acid and glacial acetic acid for 1/3 hour, and there was formed isoborneol $[\alpha]_D$ −10.56°. During this reaction, as the time of reaction was prolonged, the

(23) A. Reychler, *Ber.*, **29** (1896), 696.

rotatory power decreased gradually; and after the elapse of 110 hours the isoborneol obtained was quite inactive.

Camphene $[\alpha]_D+8.28°$ when treated separately with 50% sulphuric acid and glacial acetic acid, gave camphene of $[\alpha]_D+5.20°$ in the former case and of $[\alpha]_D+6.22°$ in the latter; while isoborneol $[\alpha]_D\pm0°$ was formed when treated with the mixture of the two acids. Further, isobornyl acetate $[\alpha]_D-47.81°$ was treated with 50% sulphuric acid, glacial acetic acid, and their mixture. When each of the acids was used separately, no appreciable change in the rotatory power of the ester was seen although the reaction was continued for 3 hours; however, when the acid mixture was used, even after the reaction of only 1/3 hour, there was seen appreciable change in the rotatory power of the ester, and the longer the time of reaction, the more remarkable was the change.

Conclusion.

Camphor, when reduced, forms borneol and isoborneol, and both of them change into camphor when oxidised. Camphor and epicamphor form mainly borneol and alcohol of borneol type respectively when reduced with metallic sodium and alcohol, and mainly isomeric alcohol corresponding to it when reduced with metallic catalyser and hydrogen, while nor-camphor in these cases gives constantly alcohol of isoborneol type as a main product. On the other hand, dimethylcamphor always forms alcohol of borneol type as a reduction product due to the asymmetric synthesis.[24]

Vavon[25] has inferred that by the reduction of camphor, isoborneol is formed, which is soon transformed in to borneol. This inference of Vavon that isoborneol is transformed into borneol was confirmed by the writer's experiment, and it was also recognized, conversely, that borneol may be transformed into isoborneol. This fact that isoborneol is as well transformed to borneol as it is formed from borneol, is also explained by the result of determination of the heats of combustion of both of these compounds. However, from these values of heat of combustion, it will be considered that borneol 1489.3 Kcal is at first formed which changes into isoborneol 1472.5 Kcal. The proportion of diastereoisomers of alcohol thus formed by the reduction of camphor depends on the mobility of hydrogen in α-position caused by the process and condition of the reduction. It was observed that the velocity of the isomeric change was greatly influenced in the presence of alcohol. The intramolecular change between borneol and isoborneol was also seen, when their acetates were treated with sulphuric acid. Although borneol which was considered very difficult to convert into camphene, the transformation was easily effected by using dehydrating agent such as alumina or $H_2SO_4.3H_2O$. Bornyl acetate forms camphene as well as isobornyl acetate by the action of $H_2SO_4.3H_2O$, and it is an interesting phenomenon that dimethylborneol, when dehydrated, forms hydrocarbons of not only the camphene form but also the bornylene form.

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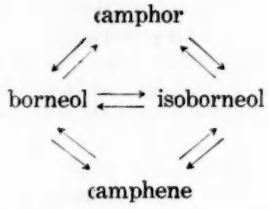
(24) J. H. Van't Hoff, Die Lagerung d. Atome in Raum, 1894, 30.
(25) Vavon and Peignier, Bull. soc. chim., [4] 39 (1926), 666, 924.

When camphene is treated with 50% H_2SO_4 and glacial acetic acid, borneol as well as isoborneol is formed. Therefore, it is supposed[26] that there is the following chemical relation between camphor, borneol, isoborneol, and camphene.



The fact that in the course of the dehydration of borneol and isoborneol inactive camphene was formed, was explained by some investigators[27] that when borneol and isobroneol are changed to camphene, an isomer, named camphene hydrate, is formed which converts itself to the racemic compound. That, during the change from camphene to isoborneol by hydration, camphene hydrate is formed as an intermediate product is quite acceptable, but with regard to the racemisation of camphene hydrate, it is rather inconceivable from the standpoint of stereochemistry and only a future investigation will explain it. (*To be continued*).

On the Catalytic Action of Japanese Acid Earth. XI*. The Isomerisation of Aldehydes to Ketones and the Explanation of the Migration of the Radicals from the Standpoint of the Electronic Theory.

By Koshiro ISHIMURA.

(Received May 14, 1941.)

Introduction. S. Daniloff[1] first observed that di- or trisubstituted acetaldehydes are partly transformed into the corresponding ketones, when warmed with acidic substances such as dilute sulphuric acid or a mixture of hydrochloric and acetic acids, or when treated with phosphorus pentachloride at ordinary temperature, while they are completely changed

(26) cf. Meerwein and Van Ernster, *Ber.*, **53** (1920), 1815; *ibid.*, **55** (1922), 2500.

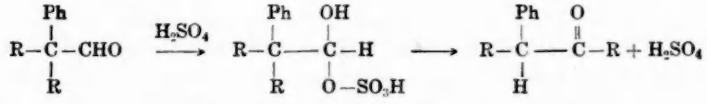
(27) J. Bredt, *J. prakt. Chem.*, **131** (1931), 137; J. Houben and E. Pfankuch, *Ann.*, **489** (1931), 193.

* X., this Bulletin, **10** (1935), 1

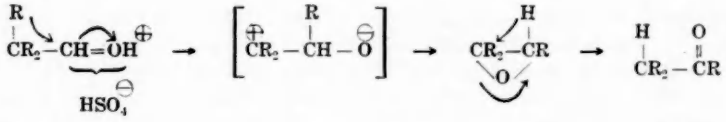
(1) *J. Russ. Phys. Chem. Soc.*, **49** (1917, 282; *ibid.*, **51** (1919), 97; *ibid.*, **57** (1925), 428; *Ber.*, **59** (1926, 377; *ibid.*, **60** (1927), 2390; S. Daniloff and E. Venus Danilova, *Ber.*, **59** (1926), 1032; *ibid.*, **60** (1927), 1050; *ibid.*, **62** (19.9), 2658; *ibid.*, **63** (1930), 2269, 2765; E. Venus Danilova, *Ber.*, **61** (1928), 1954.

into ketones by the action of concentrated sulphuric acid at about −10°C. The oximes of the aldehydes also yield ketones on heating with dilute sulphuric acid, but in this case the reaction product contains a certain quantity of the original aldehydes. Similar facts were observed by A. Orekhoff and M. Tiffeneau.[2] Later M. Tiffeneau[3] has studied extensively with his collaborators along this line, aiming to explain the relation between the "migratory tendency" and "capacity of affinity" of various organic radicals. They seem to hold the view that the migratory tendency as well as the capacity of affinity of organic radicals is a certain definite property of each radical and they concluded that a parallel relation does not always exist between these two properties. M. Migita[4] studied the pinacolinic rearrangement as a method of determining the relative electronegativities of organic radicals. He explained lucidly the facts observed by himself and others from the standpoint of the electronic theory of valency, which have previously been regarded apparently contradictory and not interpreted satisfactorily.

It appears, as J. W. Baker[5] suggested, that the rearrangement of the aldehydes mentioned above results from the actual interaction between the aldehydes and the strong acidic substances, giving rise to certain intermediate compounds, which are subsequently decomposed into the ketones isomeric to the original aldehydes. Thus in the presence of sulphuric acid the initial stage of the isomerisation may be the addition of a molecule of sulphuric acid to the aldehyde and the resulting sulphuric ester of the glycol may then undergo an ordinary pinacolinic rearrangement so as to give the ketones.



Another explanation was given by C. W. Shoppee[6] who suggested that sulphuric acid may function in the conversion of the carbonyl oxygen into the type of an oxonium salt, the attraction of positive charge so formed initiating the necessary electronic displacements resulting in the formation of an ethylene oxide, which then undergo a further pinacolinic change.



Different mode of combination may be possible, however, between aldehydes and the acidic reagents according to the nature of the latters.

(2) *Compt. rend.*, **182** (1926), 67.
(3) *Bull. soc. chim.*, **49** (1931), 1595–1860 (twenty-two papers).
(4) *This Bulletin*, **3** (1928), 308; *ibid.*, **4** (1929), 57, 225; *ibid.*, **7** (1932), 334, 341, 377, 382; *ibid.*, **8** (1933), 22, 27.
(5) Baker, "Tautomerism", (1934), 292.
(6) Thesis, London, 1929; (Baker, "Tautomerism", 1934, 292).

Consequently the intermediate compounds thus formed may have different intramolecular structures and show different chemical behaviours. It is clear that the subsequent decomposition of such an intermediate compound may take a different course giving rise sometimes to one and sometimes to other ketone, isomeric to each other, depending on the reagent as well as on the experimental conditions.

There is another type of reaction leading to the same isomerisation, i.e., isomerisation by thermal effect in the presence of catalysts. It was observed for the first time by Ramart-Lucas[7] and her collaborators. They distilled polysubstituted ethylene glycols, ethylene oxides and acetaldehydes over diatomaceous earth at different temperatures ranging from 200 to 600°C. under the reduced pressure of about 10 mm., and obtained various types of ketone, aldehyde, and hydrocarbon. The kinds and structures of these reaction products were found to depend chiefly upon the reaction temperature. They used the ultraviolet absorption spectra of these compounds for the study of the molecular rearrangement, and found that the "ascending branch" of the absorption curve of the more stable substance lies always nearer to the visible part than that of the less stable, when a rearrangement of a less stable substance into a more stable one takes place, preceded or followed by the elimination of a molecule of water, acid or salt. Thus the "ascending branch" of the absorption curve of glycol is placed farthest and that of the corresponding ketone nearest to the visible part, while that of aldehyde lies in an intermediate position; and hydrocarbon of the related structure, if produced, will exhibit its absorption curve with an "ascending branch" lying nearest to the visible part. Of the two isomeric ketones the one more stable at higher temperature always shows deeper absorption than the less stable. Thus it is a natural course, according to their opinion, that glycols are converted by thermal effect successively into aldehydes, ketones, and hydrocarbons. They further supposed that the study of the absorption spectra in the ultraviolet region would, therefore, enable them to predict which ketone will be produced from a certain aldehyde when there is a possibility of obtaining two isomeric ketones. No actual example of isomerisation of this type was, however, given by them so far as the author knows.

S. Daniloff[8] also observed the same type of isomerisation in the cases of substituted acetaldehydes, which were easily transformed into the isomeric ketones by thermal effect; thus by passing aldehydes over anhydrous aluminium sulphate heated at about 350°C. he obtained ketones isomeric to the aldehydes, and reasonably remarked[9] that it is natural that the less stable aldehydes may isomerise into the more stable ketones, that is to say, a substance with greater heat of combustion isomerises into that with the smaller.

In the present research a number of disubstituted acetaldehydes have been newly synthesised and subjected to isomerisation into the corresponding ketones in order to find which ketone of the two possible isomers

(7) *Compt rend.*, **186** (1928), 1301; *ibid.*, **186** (1928), 1626, 1848; *ibid.*, **188** (1929), 638, 1301; *Bull. soc. chim.*, **45** (1929), 478, 718; *ibid.*, **49** (1931), 1860.
(8) *J. Russ. Phys. Chem. Soc.*, **62** (1929), 723.
(9) *Ber.*, **60** (1927), 1056.

will thereby be produced, and the results have been explained from the standpoint of the electronic theory of organic compounds.

The isomerisation was carried out in the presence of Japanese acid earth. Its catalytic action at high temperatures has already been investigated by Dr. H. Inoue and the present author[10] on various organic compounds, and has been shown to be far stronger than those of alumina and silica, the chief components of the acid earth. It was also confirmed by the present author* that the existence of water in addition to the two components is indispensable for the characteristic catalytic action of the earth, and was suggested that these three components must be suitably oriented on the surface of the earth in order to form the catalytically "active centres." When a molecule of an organic compound is adsorbed on the "active centre" thus formed, it must also be oriented suitably on this centre in order to get activated. The interatomic bonds of a molecule thus adsorbed on an active centre, will consequently be weakened and the atoms will rearrange themselves within the molecule so as to gain a more stable structure, leading to the observed transformation.

Experimental Procedure. *Conditions of the Experiment and Manupilation.* The middle part convering 33 cm. of a Jena glass tube with an inner diameter of 1.5 cm. was filled with granules of Japanese acid earth with diameters from 1.5 to 3.0 mm.. The tube was heated at 300°C. and maintained at that temperature during the experiment in a horizontal electric furnace slightly inclined, and then the aldehyde was passed into it drop by drop with a rate from 3 to 4 g. per hour. A slow flow of carbon dioxide through the tube served to prevent the oxidation of the aldehyde by atmospheric oxygen and to carry away the reaction products. A receiver connected with the end of the tube was cooled with ice water to collect the reaction products. When all of the aldyhyde was passed in and no more reaction product (i) was observed to come out of the tube, the receiver was changed and the whole reaction system was evacuated, the temperature being maintained at 300°C meanwhile, and some more product (ii) was obtained. The receiver was again changed and the temperature was raised to 350°C. under the reduced pressure and a further portion of the product (iii) was obtained. The product (i) usually consisted of an easily flowing colourless liquid (mainly hydrocarbon) mixed with water drops, while the products (ii) and (iii) were for the most part colourless or yellowish fragrant viscous oils which solidified on cooling to crystalline masses. In some cases the temperature of the reaction tube was finally raised to 450°C under the reduced pressure and a reddish brown viscous oil mixed with a small quantity of crystals was obtained. Each product was separately subjected to suitable treatments to isolate and identify the individual substances contained in it, and to estimate their relative quantities.

Confirmation and Analysis of the Reaction Products. In every case no trace of the aldehyde unchanged was found to exist in the reaction

(10) H. Inoue, this Bulletin, **1** (1926), 157, 177, 197, 219; H. Inoue and K. Ishimura, *ibid.*, **9** (1934), 423, 431; K. Ishimura, *ibid.*, **9** (1934), 493, 522; *ibid.*, **10** (1935), 1.

* *Loc. cit.*

products. The ketones produced by the isomerisation were mostly obtained as solid crystalline mass. Their constitutions were confirmed by the Beckmann rearrangement of their oximes on one hand and by synthesis on the other, as described below.

When two isomeric ketones were formed simultaneously by the isomerisation of one aldehyde, the exact analysis of the experimental results became sometimes very difficult, for the isolation of both the ketones followed by the estimation of their relative quantities was not an easy work. A simple thermal analysis carried out beforehand proved very useful in such cases. Equilibrium diagrams of the systems of phenyl-*p*-methylbenzyl ketone and *p*-tolylbenzyl ketone and of *p*-chlorophenyl-*p*-methylbenzyl ketone and *p*-tolyl-*p*-chlorobenzyl ketone were drawn, which much helped to determine the compositions of the reaction mixtures. Rheinboldt's method[11] was modified for this purpose; definite quantities of the two compounds synthesised and purified by appropriate methods were intimately mixed, molten, crushed and pulverised after cooling and put in small capillaries of about 40 mm. in length and from 1 to 2 mm. in diameter. The determination of the thawing as well as melting points was carried out in the same manner as the molecular weight determination by Rast's method. Reliable results were obtained as well without stirring the content of the capillary with a slender glass rod inserted into it, as proposed by Rheinboldt. Thus a very small quantity of materials was enough to complete one series of experiment and the time required for the determination was considerably shortened.

As shown in Fig. 1 and 2 it has been found by the author that a eutectic point exists in the system of phenyl-*p*-methylbenzyl ketone and

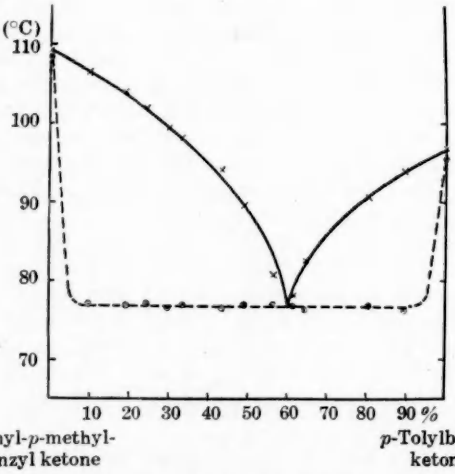


Fig. 1. Equilibrium diagram of the system: phenyl *p*-methylbenzyl ketone and *p*-tolylbenzyl ketone.

(11) *J. prakt. Chem.*, [2] **111** (1925), 242; *ibid.*, **112** (1926), 187; *ibid.*, **113** (1926), 199. Pfeiffer, "Organische Molekülverbindungen", (1927) 66-85.

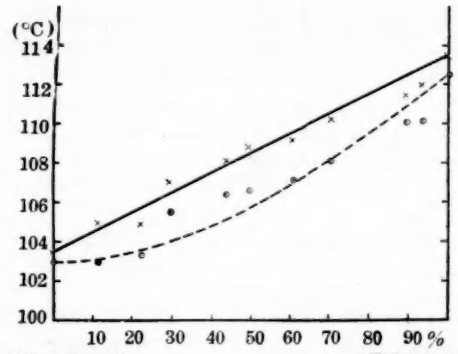


Fig. 2. Equilibrium diagram of the system: *p*-chlorophenyl-*p*-methylbenzyl ketone and *p*-tolyl-*p*-chlorobenzyl ketone.

p-tolylbenzyl ketone, while in that of *p*-chlorophenyl-*p*-methylbenzyl ketone and *p*-tolyl-*p*-chlorobenzyl ketone a diagram characteristic to solid solution has been obtained.

Materials and Products. The aldehydes employed in the present experiment were synthesised according to the general scheme shown below:—

$$\underset{(I)}{Ar{-}CO{-}CH_2Br} \rightarrow \underset{(II)}{Ar{-}CO{-}CH_2{-}O{-}CO{-}CH_3} \rightarrow \underset{(III)}{Ar{-}CO{-}CH_2{-}OH} \xrightarrow{(Ar'MgI)}$$

$$\underset{(IV)}{Ar_2C(OH){-}CH_2{-}OH} \rightarrow \underset{(V)}{Ar_2CH{-}CHO} \rightarrow \underset{(VII)}{Ar_2CH{-}COOH}$$

$$\downarrow$$

$$\underset{(VI)}{Ar{-}CO{-}Ar'}$$

ω-Bromacetophenone and ω-bromo-*p*-methylacetophenone (I) were interacted with potassium acetate in alcoholic solution giving the corresponding acetates (II), which on hydrolysis by boiling with barium carbonate were changed respectively to benzoyl carbinol and *p*-methylbenzoyl carbinol (III). By Grignard reaction with aryl magnesium iodide they gave α, α'-diaryethylene glycols (IV) which suffered intramolecular rearrangement accompanied by the splitting of a molecule of water, when heated at about 115°C. with crystalline oxalic acid mixed with a small quantity of water for three hours, or when heated at about 180°C. for several hours, with a mixture of water and a few drops of concentrated sulphuric acid in a sealed tube, resulting in the formation of the required aldehydes (V).

The constitutions of the glycols and the aldehydes were confirmed by oxidising them to diaryl ketones (VI) and diarylacetic acids (VII) respectively.

The ketones produced by the isomerisation of the aldehydes were identified by the Beckmann rearrangement of their oximes on one hand and by synthesis on the other, as schematically shown below:—

$$\mathrm{Ar{-}CH_2{-}CO{-}Ar'} \rightarrow \underset{\text{(VIII)}}{\mathrm{Ar{-}CH_2{-}C(=NOH){-}Ar'}} \rightarrow \underset{\uparrow\ \text{(IX)}}{\mathrm{Ar{-}CH_2{-}CO{-}NH{-}Ar'}}$$

$$\mathrm{Ar{-}CH_2{-}COOH + NH_2{-}Ar'}$$

$$\underset{\text{(X)}}{\mathrm{Ar{-}CH_2{-}Br}} \rightarrow \underset{\text{(XI)}}{\mathrm{Ar{-}CH_2{-}CN}} \rightarrow \underset{\text{(XII)}}{\mathrm{Ar{-}CH_2{-}COOH}} \rightarrow \underset{\text{(XIII)}}{\mathrm{Ar{-}CH_2{-}CO{-}Cl}}$$

$$\xrightarrow{(CH_3{-}C_6H_5)} \underset{\text{(XIV)}}{\mathrm{Ar{-}CH_2{-}CO{-}Ar'}} \leftarrow \underset{\text{(XV)}}{\mathrm{Ar{-}CH_2{-}CN}} + \mathrm{BrMgAr'}$$

The oxime (VIII) of the ketone was dissolved in dry ether and phosphorus pentachloride was added little by little, and the reaction product was poured into ice water, and the solid mass separated was purified by recrystallisation from alcohol, which was identified with the product (IX) obtained by the interaction between arylacetic acid and arylamine.

Tolyl and xylyl bromides (X) were converted successively into cyanides (XI), carboxylic acids (XII) and acid chlorides (XIII) which were condensed with toluene in the presence of anhydrous aluminium chloride, thus the required ketone (XIV) were synthesised. The ketones were also obtained from arylacetonitriles (XV) by the action of aryl magnesium iodide. A third method of obtaining the same ketone is the oxidation of diarylcarbinol (XIX) produced from arylacetaldehyde (XVIII) by the Grignard reaction, which was in its turn produced by heating arylethylene glycol (XVII) at about 180°C for four hours in a sealed tube with water and a few drops of concentrated hydrochloric acid.

$$\underset{\text{(XVI)}}{\mathrm{Ar{-}CO{-}CH_2{-}OH}} \rightarrow \underset{\text{(XVII)}}{\mathrm{Ar{-}CHOH{-}CH_2{-}OH}} \rightarrow \underset{\text{(XVIII)}}{\mathrm{Ar{-}CH_2{-}CHO}}$$

$$\xrightarrow{(\mathrm{Ar'MgI})} \underset{\text{(XIX)}}{\mathrm{Ar{-}CH_2{-}CHOH{-}Ar'}} \rightarrow \mathrm{Ar{-}CH_2{-}CO{-}Ar}$$

The arylethylene glycol (XVII) was obtained by the catalytic hydrogenation of aroylcarbinol (XVI) under the ordinary pressure with colloidal platinum as catalyst.

Purification of m-*Tolyl*-p-*Tolyl Acetaldehyde*. It has been observed by the present author that a large quantity of *m*-tolyl-*p*-tolyl ketone was sometimes produced when the purification of *m*-tolyl-*p*-tolyl acetaldehyde was carried out through its addition compound with sodium bisulphite or when it was oxidised to the corresponding acid with moist silver oxide. Similar facts have been also observed in the case of *p*-tolyl-*p*-chlorophenyl acetaldehyde. The mechanism of the reaction is for the time left open. F. W. Semmler[12] observed that enolacetates of aldehydes of the types

(12) *Ber.*, **42** (1909), 588, 962; *ibid.*, **43** (1910), 1724, 1890.

RCH_2CHO and $RRCHCHO$ are changed to the acid RCO_2H and the ketone RCOR respectively when oxidised with ozone or permanganate.

Separation of o- and p-*Isomers of Xylyl Derivatives.* As the starting materials for the synthesis of ketones of the type $ArCH_2COAr'$ the three isomers of xylene were used as mentioned above (p. 202), each of which usually contains small quantitis of its isomers as impurities. According to P. Hill and W. F. Short[13] the pairs of *o*- and *p*-isomers of xylyl chlorides, alcohols, acetates as well as cyanides boil at the same temperature and cannot be separated by fractional distillation, whilst *o*- and *p*-tolylacetic acids form a continuous series of solid solutions. On the contrary, the present author has found that the corresponding acid amides can be easily separated from each other by fractional crystallisation from boiling water and the purification of the related substances was always carried out quite well at this stage of preparation.

Autoxidation of Ketones of the Type $ArCH_2COAr'$. The ketones of the type $ArCH_2COAr'$ such as *o*-tolyl-*p*-methylbenzyl, *m*-tolyl-*p*-methylbenzyl, *p*-chlorophenyl-*p*-methylbenzyl and *p*-tolyl-*p*-chlorobenzyl ketones have been found to be converted largely into the mixtures of the corresponding arylacetic acids, on standing in the presence of light and air for several months. Similar facts were observed by E. C. Fortey[14] and by S. S. Jenkins.[15]

Results of Isomerisation Experiments. Four diarylacetaldehydes were employed in the present work. They were subjected to the intramolecular rearrangement in the presence of Japanese acid earth under the conditions stated above and all gave the corresponding ketones.

$$\begin{matrix} Ar \\ Ar' \end{matrix}\!\!>\!CH{-}CHO \longrightarrow ArCH_2{-}CO{-}Ar' + Ar'CH_2{-}CO{-}Ar$$

(1) Phenyl-*p*-tolyl acetaldehyde has given phenyl-*p*-methylbenzyl ketone exclusively, in other words, only the phenyl group has migrated.

(2) *m*-Tolyl-*p*-tolyl acetaldehyde has given *m*-tolyl-*p*-methylbenzyl ketone exclusively, that is only the *m*-tolyl group has migrated.

(3) *o*-Tolyl-*p*-tolyl acetaldehyde has given a mixture of *o*-tolyl *p*-methylbenzyl and *p*-tolyl-*o*-methylbenzyl ketones. The ratio of the yield in the former ketone to that in the latter was found to be about 4:1, showing that in this case the *o*-tolyl group has a migratory tendency about four times as large as that of the *p*-tolyl group.

(4) *p*-Tolyl-*p*-chlorophenyl acetaldehyde has been changed mainly to *p*-chlorophenyl-*p*-methylbenzyl ketone accompanied by a small quantity (about one tenth of the foregoing ketone) of *p*-tolyl *p*-chlorobenzyl ketone, showing that the *p*-chlorophenyl group has a very large migratory tendency in comparison with the *p*-tolyl group in this case.

Thus these results clearly show that the order of the migratory tendency of the aryl groups is as follows:—

Phenyl, *m*-tolyl>*p*-chlorophenyl>*o*-tolyl>*p*-tolyl.

(13) *J. Chem. Soc.*, **1935**, 1126.
(14) *J. Chem. Soc.*, **75** (1899), 871.
(15) *J. Am. Chem. Soc.*, **57** (1935), 2733.

Discussion of the Results. *Nature of the Catalyst in the Isomerisation.* Japanese acid earth employed as catalyst in the present experiment is a kind of clay abundantly produced in many districts in Japan. It resembles Fuller's earth and Florida earth in many respects and is essentially a certain type of hydrated aluminium silicate mixed with colloidal silica[16] and small amounts of many other metallic oxides. Its average composition is as follows:—

SiO_2, 60–72; Al_2O_3, 13–20; Fe_2O_3, 2–4; CaO, 0.5–2; MgO, 1–5; K_2O+Na_2O, 0.5–1.8; ignition loss, 7–15%.

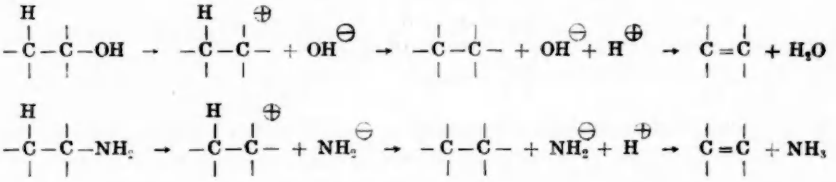
The earth is designated "acid" because it turns a blue litmus paper red when placed on the paper and moistened with a few drops of water. But the colour change is restricted only to the neighbourhood of that part of the paper which is directly in contact with the earth. This phenomenon was explained as due to its characteristic selective adsorptive power for hydroxyl ion.[17] The earth also manifests various oxydase-like colour reactions, e.g. the reactions for indophenol, potassium iodide, leuco-base of malachite green and benzidine.[18] When suspended in the water solution of pyrogallol the earth oxidizes it gradually.[19] Cane sugar and starch are hydrolysed into invert sugar[20] and maltose[21] respectively, when their water solutions are shaken with the earth. All these reactions also, the author believes, may be ascribed to the hydrogen ion generated as the result of the selective adsorption mentioned above.

In dry state, especially when dehydrated at 200–300°C., the earth adsorbes ammonia, vapours of water, alcohols, ketones, ethers, etc.. The adsorption of these vapours takes place very strongly, sometimes with the evolution of considerable quantity of heat, the adsorbates being retained tenaciously on it.[22] At high temperature, water or ammonia is eliminated from the organic adsorbates when the organic molecules contain hydroxyl or amino group, and the dehydration or deamination is accompanied very often by intramolecular rearrangements. Thus cyclohexanol and their methyl derivatives have been found to produce cyclohexene and its methyl derivatives together with methylcyclopentane and dimethylcyclopentanes respectively,[23] when passed on the earth heated at 300–350°C. Cyclohexylamine and its methyl derivatives have similarly given cyclopentane series,[24] showing that the six-membered carbon ring was converted into the five-membered one.

The elimination of water or ammonia may be induced by the initial attraction of hydroxyl or amino group towards the earth, and these negative groups tend to be ionized and will be splitted as anions. If the remain-

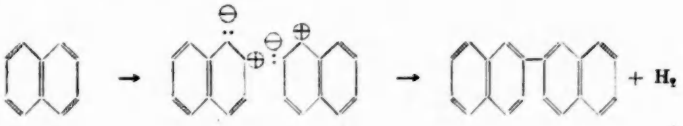
(16) K. Yamamoto, *J. Soc. Chem. Ind. Japan*, **34** (1931), 244B; *ibid.*, **36** (1933), 38B, 460B.
(17) Y. Tanaka and T. Kuwata, *J. Soc. Chem. Ind. Japan*, **32** (1929), 290B; Y. Tanaka, T. Kuwata and S. Furuta, *ibid.*, **35** (1932), 224B.
(18) K. Kobayashi and K. Yamamoto, *ibid.*, **26** (1923), 29B.
(19) H. Kaneko, *J. Chem. Soc. Japan*, **45** (1924), 189.
(20) T. Okuno, *J. Soc. Chem. Ind. Japan*, **28** (1925), 54B.
(21) B. Kato, J. Zymurgy (in Japanese), **2** (1924), 1023.
(22) K. Ishimura, this Bulletin, **10** (1935), 2.
(23) H. Inoue, *loc. cit.*
(24) K. Ishimura, *loc. cit.*

ing positively charged fragment has a hydrogen atom attached to it, it can be stabilised by the loss of a proton which then unites with the splitted anion to form water or ammonia molecule, as schematically shown below:—



When the removal of a proton occurs at α-carbon atom with respect to hydroxyl or amino group as shown above, cyclohexane series will be produced. But if it occur at β-carbon atom the molecular rearrangement will take place resulting in the formation of cyclopentane series.

H. Inoue and the present author[25] have formerly found that when a mixture of naphthalene and some dry powdered Japanese acid earth is heated at about 300°C. in a sealed tube, a marked amount of a resinous matter is produced, which is mainly composed of β, β'-dinaphthyl. The formation of β, β'-dinaphthyl from naphthalene by the catalytic action of the earth may be explained similarly: by the electron-attracting property of the earth the molecule of naphthalene is polarized[26] and an unshared electron pair is placed on that carbon atom which is attracted by the earth, leaving positive charge on some other carbon atom. When another molecule of naphthalene comes into the force field of the molecule thus polarized, it will, according to the author's opinion, in turn be polarized and in consequence the combination of the proton and the hydrogen anion will take place to produce a hydrogen molecule, accompanied by the formation of the dinaphthyl. There are equal chance for α- and β-positions thus to be polarized, but the effect of steric hindrance will lead to the formation of β, β'-dinaphthyl exclusively. The process may be given as follows:—

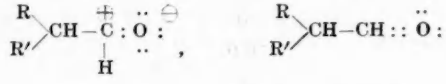


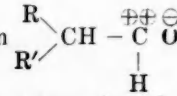
It is therefore very reasonable to admit that the essential function of Japanese acid earth as catalyst is that of attracting unshared electron pairs in the molecules of adsorbates to form co-ordinate links with certain positive centres situated on the surface of the earth, probably with silicon or aluminium atom or both. At least the fundamental action of the earth must consist in bringing a positive potential into the molecules adsorbed on it.

(25) This Bulletin, **9** (1934), 432.
(26) L. Pauling, "The Nature of the Chemical Bond," (1940), 152.

Mechanism of Isomerization. When a molecule of disubstituted acetaldehydes RR'CHCHO approaches to the surface of the earth, an unshared electron pair of the carbonyl oxygen is attracted by the earth.

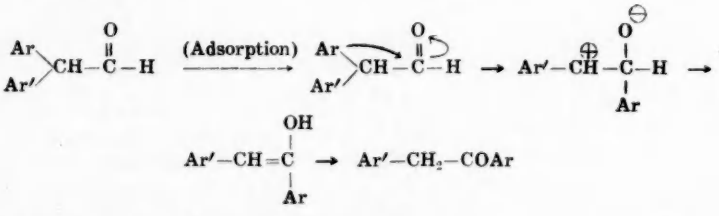
Now in normal state the resonance between the structures



(with a very small contribution from ) takes place in the aldehyde molecule, and evidences are given that the amount of the ionic character (single bond character) of the carbonyl carbon is about 50 percent, by the measurement of electric dipole moments of various ketones and aldehydes as well as by the electronegativity difference for carbon-oxygen bond.[27] But in the adsorbed molecule of an aldehyde the electronic distribution within the molecule is disturbed, and consequently an electronic displacement of electrons in the carbonyl group $\overset{\frown}{C{=}O}$ will be promoted, so that the single bond character of the carbon-oxygen link is greatly enhanced, leaving the carbon atom with an open sixtet of electrons, and the resonance is destroyed.

In this activated state the depletion of the octet round the carbonyl carbon atom necessitates the migration of an anion towards it from the adjacent α-carbon atom. The demand for negative charge of the α-carbon atom, from which the anion is detached, will then cause the splitting of a proton from the carbonyl carbon followed by the flow of electron pairs from the latter carbon atom towards the former. If it is a hydrogen atom that is first removed as anion from the α-carbon atom, there would take place only the wandering of two hydrogen atoms exchanging their positions of attachment, and thus no actual rearrangement would occur. But if one of the aryl groups migrates with its valency electrons, the proton splitted from the carbonyl carbon will unite with the oxygen, so that a ketone will be produced in the enolic form.

The rearrangement visualized as above will occur according to the following scheme:—



In the systems otherwise identical, as in the present case, it is to be expected that the tendency to migration of different anions would follow their order of anionic stability. As it is generally accepted, the hydrogen

(27) L. Pauling, *loc. cit.*, 152.

anion is very unstable, and one of the aryl groups, therefore, will be separated. Which of the two aryl groups, then, will be separated first is, determined by the magnitude of their capacity for electron-attraction; the more electron-attracting group will more easily be separated. When the capacities for electron-attraction of the two groups are not greatly different, there is the possibility of the simultaneous separation of the two groups, giving rise to a mixture of two isomeric ketones, their relative yields depending upon the relative capacity for electron-attraction of the migrating groups.

If the proton and the anion thus successively separated pass outside the force field of the rearranging molecule, they may combine directly to give rise to the formation of hydrocarbons. Thus benzene and toluene have been actually confirmed to exist in the reaction products of the present experiment in considerable quantities.

According to J. W. Baker's[28] opinion the initial stage of the rearrangement of the aldehyde by the action of sulphuric acid is possibly the addition of a molecule of the acid to the aldehyde and the sulphuric acid ester of the glycol so formed may then undergo an ordinary pinacolinic electron displacement with hydrogen migration to give the ketone. C. W. Shoppee[28] has explained the conversion, as above stated, by assuming the intermediate formation of an ethylene oxide. But in the case of the present work the mechanism involving the actual formation of either glycol or ethylene oxide as intermediates seems untenable. R. Lagrave[29] distilled under the reduced pressure a series of ethylene oxides of the general formula $(Ph)_2=\overset{O}{C}-CHR$ and obtained as the major product the ketone $(Ph)_2CH-CO-R$ but found that the considerable quantity of the aldehyde $(Ph)_2CR-CHO$ was also produced, where Ph and R represent phenyl and alkyl groups respectively. Therefore, if the transformation of an aldehyde into an isomeric ketone be effected through the intermediate formation of an ethylene oxide, there should exist an equilibrium between the aldehyde and the ethylene oxide under such conditions. No trace of either aldehyde or ethylene oxide, however, was found in the reaction product.

The experimental results obtained by Ramart-Lucas and Jean-Pierre Guerlain[30] are in good accordance with those of the present experiment. They passed aldehyde of the type ArRCHCHO over diatomaceous earth heated at 500–600°C. as above stated and obtained ketones of the type $ArCH_2COR$ as the main product together with some quantity of the unchanged original aldehydes. It is natural in the light of the consideration above given that the alkyl group R migrates in preference to the aryl group Ar, since it has a smaller capacity for electron-release. The reaction temperature was, however, by far higher than in the case of the present experiment and yet there remained a portion of aldehyde unchanged. These facts may be explained by the weaker activity of the catalyst, in other words, by the smaller capacity for electron-attraction of diatomace-

(28) "Tautomerism", (1934), 292.
(29) *Ann. chim.*, [X], **8** (1927), 363.
(30) *Bull. soc. chim.*, **45** (1929), 478, 718; *ibid.*, **49** (1931), 1860.

ous earth in comparison with Japanese acid earth. The far weaker catalytic activity of the former than that of the latter has been shown by the present author[31] by comparing the activitiy for producing β, β'-dinaphthyl from naphthalene.

Comparison of the Capacity for Electron-release of the o- *and* p-*Tolyl Groups.* As above stated, in the author's experiment, when diarylacetaldehydes rearrange into the corresponding ketones, phenyl-, *o*-tolyl-, *m*-tolyl and *p*-chlorophenyl radicals migrate in preference to the *p*-tolyl radical, showing that the last mentioned possesses the greatest capacity for electron-release.

Since the methyl group tends to produce an effect of electron-release relative to hydrogen, when it is attached to the benzene nucleus, it loses electrons to the ring; they go mainly to the ortho and para carbon atoms. This capacity of the methyl group to repel electrons has been regarded as due to its inductive effect only and the tautomeric effect of the methyl group is inconceivable from the standpoint of ordinary organic chemical theory. J. W. Baker and W. S. Nathan[32] suggested, however, that the methyl group, when directly attached to a conjugated system, is capable of permitting electron-release by a mechanism which is assumed to function in addition to the inductive effect and in essentials is of the type of tautomeric effect $H\text{–}\overset{\frown}{CH_2}\text{–}\overset{\frown}{C}\text{=}C\text{–}C\text{–}$ much as if the electrons were unshared as in chlorine. The inductive effect of the methyl group will thus be greatly reinforced. By applying the new idea the English authors gave a satisfactory explanation to various points till then obscure in organic chemistry and found furthermore, together with C. W. Shoppee,[33] that the new postulated mechanism is of not an electromeric but of a mesomeric (permanent) type. The definite demonstration of the reality of the tautomeric electron displacements of the electrons of nonionizing CH– groups was then made by the study of E. D. Hughes, C. K. Ingold, N. A. Taher and L. C. Bateman.[34] Recently Y. Tsuzuki, T. Uemura and N. Hirasawa[35] found that the absorption bands of *o*- and *p*-nitrosotoluenes are shifted to a longer wave length relative to that of nitrosobenzene. They ascribed the fact to the tautomeric but not inductive effect of the methyl group situated in the ortho and para positions with regard to nitroso group. They showed moreover that the methyl group in the para position exerts a much stronger effect than those in the ortho and meta positions. The results of the present work lead also to the same conclusion. Thus the *o*-tolyl group migrated to a larger degree than the *p*-tolyl group as already stated (p. 203). These results apparently contradict with the facts that in the aromatic substitution the methyl group appears to be more nearly ortho-orienting than any other.[36] It is tentatively suggested here that the smaller effect of the methyl in the ortho position or the greater ease with which the *o*-tolyl group separates as anion may be

(31) This Bulletin, **9** (1934), 498.
(32) *J. Chem. Soc.*, **1935**, 1844.
(33) *Ibid.*, **1935**, 1847.
(34) *J. Chem. Soc.*, **1940**, 949, and subsequent papers.
(35) *J. Chem., Soc., Japan*, **61** (1940), 1063.
(36) J. B. Rease, *Chem. Reviews*, **14** (1934), 77.

ascribed to the formation of hydrogen bond between hydrogen in the methyl and carbonyl (or nitroso) oxygen: it is very probable that an alkyl group can form a hydrogen bond, provided that an electron-donating atom is suitably placed with respect to it.

Comparison of the p-Tolyl and p-Chlorophenyl Radicals. A greater resistance of the *p*-tolyl (and *o*-tolyl) group to ionisation in comparison with the *p*-chlorophenyl group, indicated by its smaller tendency to migration, can be explained by taking into consideration the inductive effect (+I) in the methyl group as above visualised on one hand and the well known inductive effect (−I) in chlorine atom superimposed on the electromeric effect of the opposite sign (+T) on the other. The action of the electromeric effect (+T) in chlorine atom is diminished by the inductive effect of its own, if not totally suppressed, by the flow of electrons towards it from *α*-carbon atom.

Quite recently Y. Tsuzuki, T. Uemura and N. Hirasawa[37] reached to the conclusion that the *p*-tolyl group has a greater capacity for electron-release than the *p*-chlorophenyl group by studying the effect of para-substituents to shift the absorption band of nitrosobenzene to a longer wave length. Their results accord well with that of the present work.

Comparison of the m-Tolyl and Phenyl Groups. The methyl group in the meta position exhibits a simple inductive effect but not a mesomeric effect as in the cases of para and ortho derivatives. The *m*-tolyl group shows therefore a much smaller tendency to migration, as clearly shown by the non-existence of *p*-methylbenzyl-*m*-tolyl ketone in the reaction product.

The phenyl group is capable of drawing an electric charge of either sign (±), as generally admitted, by an electromeric electron displacements of either sign (±T), when promoted by the requirement of the system. In the present case it may easily be ionised by absorbing electrons which will flow from the adjacent *p*-tolyl group. Thus the greater separability and the subsequent migration of the phenyl group may be expected in preference to the *p*-tolyl group, which actually took place.

Though the actual comparison of the relative mobility of the phenyl and *m*-tolyl groups has not been made, it is very probable that the phenyl group would be separated to a greater degree than the *m*-tolyl group owing to the inductive effect of an electron-release of the methyl group on one hand and to the inherent dual electronic character of the phenyl on the other. (*To be continued*).

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(37) *Ber.*, **74** (1941), 616.

The Synthesis of 1,4-Diphenyl-1,4-di-*p*-tolylbutatriene and 1,4-Diphenyl-1,4-di-*p*-chlorophenylbutatriene.[1]

By Osamu SIMAMURA.

(Received May 27, 1941.)

Kuhn and Wallenfels[2] synthesized tetraphenylbutatriene, which had been obtained by Brand[3] and by Salkind and Kruglow,[4] by treating tetraphenylbutynediol with phosphorus diiodide and accomplished the preparation of tetraarylhexapentaenes from hexaarylhexadiyne-(2, 4)-diols by the same procedure and later by an improved method of reducing with chromous chloride in the presence of hydrogen chloride.[5] The chemistry of these compounds, cumulenes, as Kuhn and Wallenfels call them, is of interest not only because of chemical behaviours which a system of cumulated double bonds diplays. Extending van't Hoff's model which pictures double-bonded carbon atoms by two tetrahedra sharing one edge in common, Kuhn and Wallenfels suggested that asymmetrically substituted cumulenes with an odd number of double bonds such as $R_1R_2C=C=C=CR_1R_2$ should exist in cis and trans isomerides and those with an even number of double bonds should be resolved into optical antipodes. Although the syntheses of allene derivatives in enantiomorphic isomerides[6] were verifications of van't Hoff's prediction, it may be questioned whether the model would be applicable as well to a system of many cumulated double bonds, in view of the electronic concept of valency and the mesomerism in a system of conjugated multiple bonds. A carbon atom which is bound to two neighbouring atoms by two double bonds is of the acetylene type in that it has as atomic orbitals involved in bond formation two derived from *sp*-hybridization[7] lying in a straight line extending in the opposite directions and two $p\pi$ orbitals perpendicular to the former two, the former entering into σ bonds with σ orbitals and the latter into π bonds with $p\pi$ orbitals of the two adjacent atoms. Thus the molecular structure of cumulenes may be assumed to be such that the double-bonded carbon atoms lie in a single straight line just as is the case with carbon suboxide.[8] Then, the question is to what extent the energy of the molecule depends upon the relative orientation of the substituents at one end with respect to those at the other end of the carbon atom chain. In the ethylenic linkage the single π bond makes the energy susceptible to the perturbation by the substituent groups yielding cis and trans positions of the substituents

(1) Presented on April 4, 1941, at the 63rd Annual Meeting of the Chemical Society of Japan in Tokyo.

(2) R. Kuhn and K. Wallenfels, *Ber.*, **71** (1938), 783.

(3) K. Brand, *ibid.*, **54** (1921), 1987.

(4) J. Salkind and K. Kruglow, *ibid.*, **61** (1928), 2306.

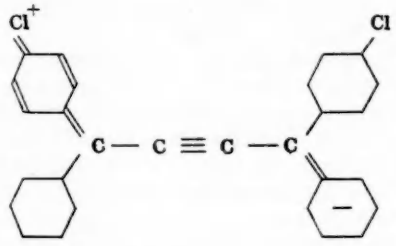
(5) R. Kuhn and K. Wallenfels, *ibid.*, **71** (1938), 1510.

(6) P. Maitland and W. H. Mills, *Nature*, **135**, (1935) 994; *J. Chem. Soc.*, **1936**, 987; E. P. Kohler, J. T. Walker, and M. Tischler, *J. Am. Chem. Soc.*, **57** (1935), 1743.

(7) Cf. J. H. Van Vleck and A. Sherman, *Rev. Modern Phys.*, **7** (1935), 205.

(8) L. O. Brockway and L. Pauling, *Proc. Natl. Acad. Sci.*, **19** (1933), 860. H. Boersch, *Monatsh.*, **65** (1935), 314.

as stable minima;[9] but in cumulenes, two p orbitals of each carbon atom being involved in bond formation, the electronic density of the bonds in the middle part of the chain may presumably be more or less symmetric with respect to the rotation around the axis of the chain and the energy



less dependent on the relative orientation of the terminal groups. Further, the intense colour of cumulenes suggests[10] a large contribution of dipolar mesomeric structures such as for example shown by the accompanying formula, and thus the double bonds acquire a single or a triple bond character considerably. It will be inferred from these considerations that the two pairs of terminal groups may rotate around the axis of the carbon atom chain with some freedom and may not be fixed in one plane contrary to the expectation from the van't Hoff model. With a view to settling this point experimentally a synthesis of cumulenes having a set of substituents which, according to the van't Hoff model, makes possible the existence of geometrical isomerides was undertaken.

The meso and racemic forms of 1,4-diphenyl-1,4-di-*p*-tolylbutynediol and 1,4-diphenyl-1,4-di-*p*-chlorophenylbutynediol were synthesized from acetylene dimagnesium bromide and *p*-methylbenzophenone and *p*-chlorobenzophenone respectively. Treatment with phosphorus diiodide converted these butynediols into desired 1,4-diphenyl-1,4-di-*p*-tolylbutatriene and 1,4-diphenyl-1,4-di-*p*-chlorophenylbutatriene. From both meso and racemic forms of each butynediol only one butatriene was obtained. If cis and trans isomerides were formed the synthetic procedure, which involved the use of phosphorus diiodide and hence the liberation of iodine in its course, may have caused the isomerization into the stabler form. By chromatographic analysis with activated alumina no identifiable compounds other than those described above were obtained. As it is a well established fact that the trans isomeride of ethylenic compounds is usually converted into the cis isomeride by irradiation with ultraviolet light, a benzene or petroleum ether solution of 1,4-diphenyl-1,4-di-*p*-tolylbutatriene was exposed to ultraviolet or sun light. It was found that decomposition of the compound took place and that when the decomposition was slight only the starting material was recovered by chromatographic separation.

Although the evidence obtained so far is not conclusive to decide between the two possibilities discussed above—which will be possible by dipole moment measurement—the synthesis may be worth reporting in

(9) E. Hückel, *Z. Physik*, **60** (1930), 423.
(10) L. Pauling, Gilman's "Organic Chemistry", 1888, New York (1938).

view of the attempted synthesis by Kuhn and Platzer,[11] who could obtain no asymmetrically substituted cumulenes in crystalline state by means of exactly the same procedue that proved successful in the case of symmetrically substituted ones.

Experimental.

1,4-Diphenyl-1,4-di-*p*-tolylbutynediols. To an ethyl magnesium bromide solution prepared from 2.4 g. of magnesium and 11 g. of ethyl bromide in 100 c.c. of ether dry acetylene was passed until no further increase of the viscous oily precipitate was observed. A solution of 15 g. of *p*-methylbenzophenone in 50 c.c. of ether was added to the acetylene dimagnesium bromide so prepared and the mixture was heated on a water bath with stirring for six hours. The reaction mixture was decomposed with dilute sulphuric acid and ice water. The ether layer was washed with aqueous sodium bicarbonate and after drying with anhydrous sodium sulphate the ether was evaporated. The remaining brown oil was brought to crystallization by rubbing with a small quantity of petroleum ether. Repeated crystallization from methanol effected the separation into two apparently pure crystalline products, one melting at 154–155.5° and the other at 145.5–151.5°, in the yields of 2.3 g. and 1.4 g. respectively. A mixture melted at 134–140°. They correspond to the theoretically expected meso and racemic forms of 1,4-diphenyl-1,4-di-*p*-tolylbutynediol. They effloresced on keeping and, as the presence of methanol of crystallization was suspected, they were recrystallized from benzene—petroleum ether mixture up to the melting points of 156–157° and 151.5° respectively. The di-*p*-chlorophenyl derivative described below was demonstrated to crystallize with one molecule of ethanol. Found for the higher melting butynediol: C, 85.9; H, 6.5; for the lower melting one: C, 86.3; H, 6.6. Calculated for $C_{30}H_{26}O_2$: C, 86.09; H, 6.20%.

Salkind and Martinsson[12] reported the synthesis of 1,4-diphenyl-1,4-di-*p*-tolylbutynediol melting at 146.° It appears to have been a mixture of the two isomerides or, if it was crystallized from alcohol, the lower melting point may be attributed to alcohol of crystallization.

1,4-Diphenyl-1,4-di-*p*-tolylbutatriene. To a solution of 1 g. of the higher melting 1,4-diphenyl-1,4-di-*p*-tolylbutynediol in 15 c.c. of dry ether was added about 1 g. of phosphorus diiodide dissolved in carbon bisulphide. The colour of the solution grew darker and suddenly yellow needles precipitated. The mixture was shaken with an aqueous solution of sodium thiosulphate and sodium hydroxide, and the crystals were collected on a filter, washed with water, and dried in a vacuum desiccator. Repeated precipitation from a hot chloroform solution by adding methanol gave lemon yellow needles melting at 236° with decomposition, yield 23% of the theory. The lower melting butynediol yielded the identical product, the mixed melting point having not been depressed. The products were combined, recrystallized from chloroform—methanol and analyzed. Found: C, 94.1; H, 6.4. Calculated for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

(11) R. Kuhn and G. Platzer, *Ber.*, **73** (1940), 1410.
(12) J. Salkind and E. E. Martinsson, *Chem. Zentr.*, **1938**, II, 3678.

1,4-Diphenyl-1,4,-di-*p*-chlorophenylbutynediols. The synthetic procedure was the same as described above for the di-*p*-tolyl derivatives. Two isomerides corresponding to the meso and racemic forms were obtained, m.p. 133–134° and 148–148.5°. Found for the higher melting butynediol: C, 73.5; H, 4.5; Cl, 15.5; for the lower melting one: C, 73.0; H, 4.4; Cl, 15.4. Calculated for $C_{28}H_{26}O_2Cl_2$: C, 73.21; H, 4.39; Cl, 15.44%.

1,4-Diphenyl-1,4-di-*p*-chlorophenylbutatriene. On treatment with phosphorus diiodide in the same manner as described for the di-*p*-tolyl derivative the above butynediols gave in the yield of 13% of the theory the corresponding butatriene melting at 246–247° with decomposition, orange yellow needles. Found: C, 79.0; H, 4.5; Cl, 16.7. Calculated for $C_{28}H_{18}Cl_2$: C ,79.06; H, 4.27; Cl, 16.67%.

The author wishes to express sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragement throughout this work.

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Physico-Chemical Investigations on Catalytic Mechanism. II. Note on The Fischer-Tropsch Synthesis of Hydrocarbons with Special Reference to its Reaction Mechanism.

By Senzo HAMAI.

(Received May 30, 1941.)

Introduction. With increasing demands for technological products, as well as from the theoretical interest in hydrocarbon chemistry in general, the synthesis of suitable hydrocarbons, especially in the line of fuel industry in the country where the sources of natural oil are lacking has become one of the most vital importance in the present time, especially, since the first publication of Fischer and Tropsch[1] was announced.

Fischer and his coworkers ever since have contributed much in establishing this into industrial scale, and besides many reports have been contributed from Professor Kita's laboratory in our country, but as far as its reaction kinetics and mechanism are concerned, the existing literatures is practically none, or at least very meagre.[2]

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(1) *Ber.*, **56** (1923), 2428.
Brenn.-Chem., **4** (1923), 276, **5** (1924), 201 (Synthol); *Brenn.-Chem.*, **7** (1926), 97, 299; *Ber.*, **59** (1926), 830, 832, 923.

(2) (a) S. R. Craxford, *Trans. Faraday Soc.*, **35** (1939), 946.
(b) E. F. G. Herington and L. A. Woodward. *Trans. Faraday Soc.*, **35** (1939), 958.

Considering such a status, we have undertaken some aspect of this investigation so as to discuss the reaction mechanism of Fischer-Tropsch synthesis of hydrocarbons and also to select good and suitable catalyst to proceed the above mentioned synthesis very effectively.

Especially the fact that the word "Catalysis" according to Schönbein, is a "Synonym" for ignorance, truly points out the exact status of the field of catalytic investigations; however, at present some noticeable progress has been made by various workers. We are not yet to be satisfied with the present condition, and we feel that there should be much done among experimentalists as well as theoreticians in this field of vital importance.

These in mind, we have carried out our experiments; the present purpose of this paper is to discuss briefly the various mechanisms so far proposed especially in reference to the recent papers of Craxford, of Herington and Woodward, and of Kodama in connection with our new mechanism recently proposed[3] in detail.

According to Craxford[2a], the primary step in this synthesis is the alternate formation and reduction of cobalt carbide to give CH_2 group, as:

$$2Co + CO + H_2 \rightarrow Co_2C + H_2O \qquad (1)$$

and with the chemisorbed hydrogen, these methylene groups are being hydrogenated into CH_4; if the formation of carbide is more rapid than its reduction, there will be very little chemisorbed hydrogen on the surface, and the CH_2 group will link to form long chains. Furthermore, the products formed are broken off as long chains on the surface by the action of the chemisorbed hydrogen. When CO is adsorbed in the outer adsorption layers and not in direct contact with the catalytic surface, its reduction leads to compounds containing oxygen, rather than hydrocarbons.

While Herington and Woodward[2b] proposed that there are two types of catalytic surfaces, namely Type A (probably cobalt carbide) which is responsible for the formation of the CH_2 groups which polymerize to the long chain hydrocarbons and Type B (probably bare cobalt metal) which through the agency of hydrogen, is responsible for the liberation of the observed products from the catalyst surface. During the reaction when (besides water) only gaseous products are formed, the centers of Type B predominate over those of Type A whereas, when liquid and solid products are produced the reverse is true.

A recent paper by Kodama and his coworkers[2c], proposed the mechanism of benzine synthesis as follows:

Firstly,

$$CO + 3M = M_2C + MO \qquad (2)$$

(2) (c) S. Matsumura, K. Tarama and S. Kodama, *Sci. Paper of Inst. Phys.-Chem. Research* **37** (1940), 302.
(d) B. Jerofejew, A. Runtzo and A. Walkowa, *Acta Physicochim.* **12** (1940), 111.
(e) F. Fischer and H. A. Bahr, *Gesamm. Abh. Kennt. Kohle*, **8** (1929), 255; O. C. Elvins and A. W. Nash, *Fuel*, **5** (1926), 263; *Nature*, **118** (1926), 154; O. C. Elvins, *J. Soc. Chem. Ind.*, **46** (1927), 473; D. F. Smith. C. O. Hawk and P. C. Golden, *J. Am. Chem. Soc.*, **52** (1930), 3221.

(3) S. Hamai, *J. Chem. Soc. Japan*, **62** (1941), 516.

and then atomic hydrogen acting on M_2C to give CH_2 and finally the longer chain hydrocarbons. As far as CO is considered it seemed quite improbable i.e., CO at the surface of catalyst with excess of H_2, Co is practically in reduced state for complete reduction of Co below 200°C. and if CO is present, reduction temperature is even lower[4].

Such reaction mechanism as Eq. (2) is another way of stating that carbon monoxide, at the surface of metal, is ruptured, and one of the components, the carbon remains as Co–C linked together (cobalt carbide) and the other component, oxygen, linked to the adjacent metal surface forming oxide of the metal which is quite improbable to be existing in such condition as,

$$\begin{array}{l} C{=}O \\ | \quad | \\ Co{-}Co{-}Co \end{array} \rightarrow \begin{array}{l} \quad C \quad O \\ \quad | \quad | \\ Co{-}Co{-}Co \end{array} \qquad (3)$$

Furthermore,

$$M + H_2O \rightleftarrows MO + H_2 \qquad (4)$$

is a reversible process, and the reaction from right to left takes place more rapidly at lower temperatures (such as 190°–200°C.); the reverse process at higher temperatures. $CO+3Co=Co_2C+CoO$ cannot be obtained in the experimental conditions of ordinary Fischer synthesis. The heat of formation of links for CO is 235.5 Kcal. while those of Co_3–C and Co–O are 9.33 Kcal. and 57.5 Kcal., respectively, so that the heat of rupture for CO molecules is enormously large as compared to those of Co_3–C and Co–O; consequently, the reaction is very improbable from the energetic consideration.

A New Mechanism Proposed. We have proposed a probable mechanism (3) of Fischer–Tropsch synthesis reaction, which we shall now elucidate in a more detailed manner.

In the case of Co type catalyst, when a $(CO+2H_2)$ mixture is passed over the catalyst, after it is throughly reduced by H_2 stream, the reaction is

$$3Co + CO \rightarrow \begin{array}{l} \quad O \\ \quad \| \\ \quad C \\ \quad | \\ Co{-}Co{-}Co \end{array} \qquad (5)$$

(i.e. adsorbed state)

which in turn act as the active center of the said reaction; then

(4) (a) Ephraim, "Inorganic Chemistry", p 357.
(b) Watanabe, *Sci. Report Tohoku Imp. Univ.* Ser. I, **22** (1933), 892. Reported the study of $CoO+CO \rightleftarrows Co+CO_2$ of which the equilibrium is practically shifted to the CO_2 side even at 563°C. and it should be completly shifted to the CO_2 side at the temperature as low as 200°C.;

$\Delta F^\circ_{200} = -10344$ cal. $\quad CO_2\% = 99.43\%$ at 563°C.
$CO_2\% = 95.87\%$ at 861°C.

$$\begin{array}{l} \overset{O}{\overset{\|}{C}} \\ \text{Co–Co–Co} \end{array} + H_2(ad) \rightarrow \begin{array}{l} \overset{OH}{\overset{|}{C\text{–}H}} \\ \text{Co–Co–Co} \end{array} \qquad (6)$$

$$\begin{array}{l} \overset{OH}{\overset{|}{C\text{–}H}} \\ \text{Co–Co–Co} \end{array} + H_2(ad) \rightarrow \begin{array}{l} \overset{H}{\overset{|}{C\text{–}H}} \\ \text{Co–Co–Co} \end{array} + H_2O \qquad (7)$$

$$\begin{array}{l} \overset{CH_2}{\overset{|}{Co}}\text{–Co–Co} \end{array} \xrightarrow{H_2(ad)} \begin{array}{l} \overset{CH_2}{\overset{|}{CH_2}} \\ \overset{CH_2}{\overset{|}{CH_2}} \\ \overset{CH_2}{\overset{|}{Co}}\text{–Co–Co} \end{array} \xrightarrow{H_2(ad)} \text{Co–Co–Co} + (CH_2)n \qquad (8).$$

Desorption

Hydrogenation

Higher Hydrocarbons ← (liquid product)

Thus, CH_2 in adsorbed state polymerize to long chain hydrocarbons on the surface of catalyst; then the desorption in presence of H_2(ad) takes place; and finally with hydrogenation reaction, the observed liquid hydrocarbons are produced.

Table 1.

Temp. °C.	$\Delta F_i°$ cal./mol.	
25°C	−34547(5)	−34356(6)
100°	−30332	−30496
200°	−24712	−25123
300°	−19092	−19568
400°	−13472	−13890
500°	− 7852	− 8123

Discussion of the Mechanism. At the initial stage of the experiment, CH_4 formation predominates, this is probably due mainly to the following reaction,

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O + 48.3\ \text{Kcal.} \qquad (9)^*$$

for which the free energy changes are tabulated in Table 1, but not through

$$\begin{array}{l} \overset{CH_2}{\overset{|}{Co}}\text{–Co–Co} \end{array} + H_2(ad) \rightarrow CH_4 + \text{Co–Co–Co} \qquad (10).$$

$\begin{array}{l} \overset{CH_2}{\overset{|}{Co}} \end{array}$—Co—Co exists comparatively in a small amount as compared with that of H_2 in the beginning of the experiment, which shows that CH_4 formation predominates through reaction (9) rather than (10). More-

(5) C. Ellis, "The Chemistry of Petroleum Derivatives" Vol. II, (1937), 1225. (G. S. Parks and Huffman, "The Free Energies of Some organic Compounds", (1932).

(6) J. Chipman, *Ind. Eng. Chem.*, **24** (1932), 1013.

(*) The fact that if the ratio $CO : H_2 = 1 : 3$ or over, CH_4 formation is very active, indicates that this recation is very reasonable. (We also confirmed this fact (2b).)

over, the fact that CH_4 formation is mainly through (9) at the initial stage is quite clearly demonstrated in our experiment, i.e., when we pumped out completely the mixed gases after a regular synthesis, and only H_2 gas was passed at 200° C. (Reaction temperature), then we confirmed that there was no formation of CH_4, contrary to what had been claimed by Craxford[2a]; but when a similar experiment was done at 300°C., we observed CH_4 formation as shown in Table 2 and Fig. 2. (CO: H_2=1: 3.18). According to the various "Carbide theory," it is explained that CH_4 formation in such a case is due to the following reaction.

$$\begin{matrix} & C \\ & | \\ Co\text{-}Co\text{-}Co \end{matrix} + 2H_2 \rightarrow CH_4 + Co\text{-}Co\text{-}Co\,, \qquad (11)$$

but in our case, as there is definitely no CH_4, it is obviously explained as:

$$\begin{matrix} & CH_2 \\ & | \\ Co\text{-}Co\text{-}Co \end{matrix} + H_2(ad) \rightarrow CH_4 + Co\text{-}Co\text{-}Co \qquad (12).$$

The reaction (12) is kinetically not observed at a temperature near 200°C., but at higher temperature (for example near 300°C.) it took place, as had been stated in our previous note[3]. This is definitely confirmed as shown in Table 2 and Fig. 2.

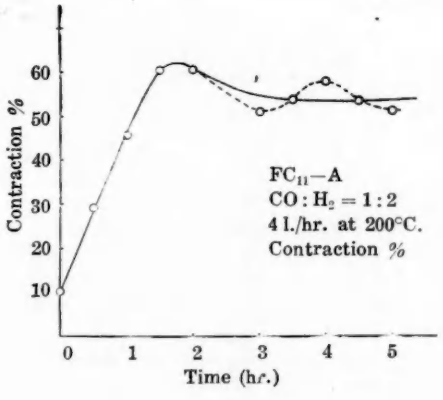


Fig. 1.

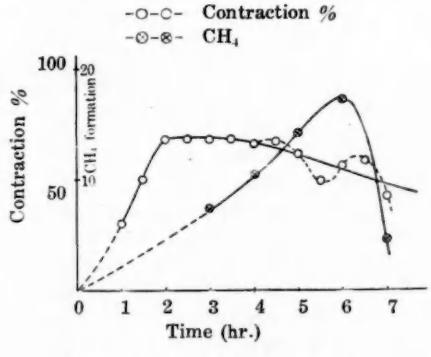


Fig. 2. FC_{11}—B CO : H_2 = 1 : 318,4 l./hr. at 200 C
Oil yield 67.5 c.c./m³

Furthermore, when we pretreated the catalyst with CO at 200°C. for 6–8 hours, and all the gases evacuated from the catalyst zone, and then only H_2 was passed, (4 l./hr.) in our desorption experiment, we observed that after certain period, CH_4 formation took place as shown in Fig. 3. (Of course, a certain time is spent for the gas to pass through the reaction vessel to the sampling part.) This time lag for CH_4 formation is probably due to the fact that CO must be desorbed before it reacts with H_2 as in Eq. (9); this in turn means that the reaction of CH_4 formation as in Eq. (9) is taking place in the gaseous phase and not on the

Table 2. Gas Analysis Data

After the regular synthesis, all the gas mixtures evacuated, and H_2 only was passed 4 l./hr. at 200°C. and 300°C.

Exp. No.	FC_{11}—A′(200°)	FC_{11}—B′(200°)	FC_{11}—I′(200°)	FC_{11}—N′(300°)
CO_2	0.2	0.2	0.2	0.1
C_2H_2	0.2	0.0	0.0	0.1
C_2H_4	0.2	0.0	0.0	0.0
CnH_{2n}	0.0	0.0	0.0	0.3
O_2	0.2	0.4	0.1	0.1
CO	0.7	0.2	0.6	0.3
H_2	96.8	96.9	96.4	93.1
CH_4	0.0	0.0	0.0	3.0
C_2H_6	0.0	0.0	0.0	0.5
N_2	1.7	2.3	2.7	2.5
Total	100.0	100.0	100.0	100.0

Table 3. Gas Analysis Data

The effect of $CO : H_2$ ratio on the CH_4 formation in the regular synthesis at 200°C. 4 l./hr.

Exp. No.	FC_{11}—A($CO : H_2 = 1 : 2$) Contraction 59%	FC_{11}—B($CO : H_2 = 1 : 3.18$) Contraction 68%
CO_2	1.8	3.8
C_2H_2	0.1	0.0
C_2H_4	0.1	0.0
CnH_{2n}	0.4	0.5
O_2	0.2	0.8
CO	29.6	5.6
H_2	56.2	58.1
CH_4	6.6(*)	17.1
C_2H_6	1.4	4.2
H_2	3.6	9.9
Total	100.0	100.0

catalyst surface. When H_2 streaming velocity was 8 l./hr. instead of 4 l./hr. and other conditions being the same, we observed that the above mentioned time lag for CH_4 formation was shortened, as expected. Hence, we may safely say that the reaction such as Eq.(9) is not occurring on the catalytic surface. A similar pretreatment was done with H_2 instead of CO, and CO only was passed after evacuation; then we found no CH_4 formation as shown in Fig. 4.

(*) CH_4 formation at the initial stage.

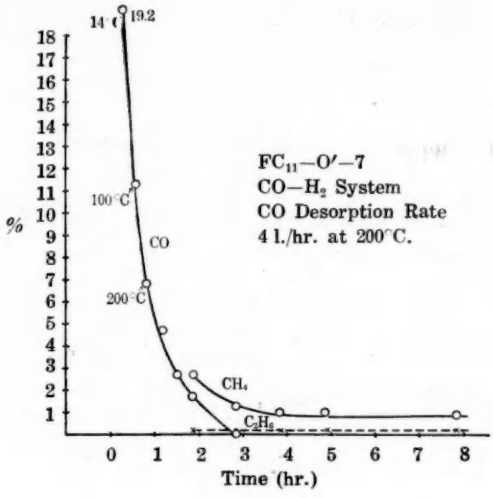


Fig. 3.

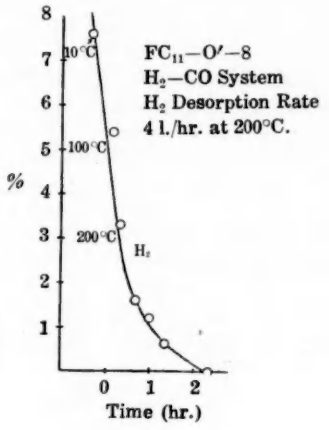
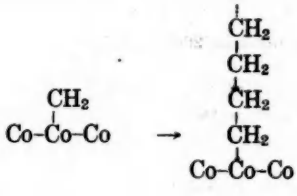


Fig. 4.

As time proceeds, the regular synthesis,



(13),

gradually becomes vigorous in parallel with the increase of Co—$\overset{\overset{CH_2}{|}}{Co}$—Co. This is quite consistent with our observation that during certain initial period practically only H_2O and CH_4 formations were recognized and no liquid hydrocarbon was observed, but after certain period (at least 5–8 hrs.), the catalytic surface might possibly have rearranged in such a way as we had conceived in our mechanism, CH_2(ad) molecules gradually increased, and the desired liquid hydrocarbon was formed.

With regard to CH_2 of which carbon is said to be in divalent state[7] and itself shows the nature of a molecule rather than a radical, and a divalent carbon quite easily passes into a trivalent state. Some of its molecular characteristics are:

Life period	5.0×10^{-3} sec. (Thermal)
	6.4×10^{-3} sec. (Photochem.)

CH_2 "Bent molecule" for which the following constants are assigned:

(7) R. F. Barrow, T. G. Person, and R. H. Purcell, *Trans Faraday Soc.*, **35** (1935), 880.

$$\nu(\sigma) = 3060 \text{ cm.}^{-1}\ ^{(8)}$$

$$\nu(\pi) = 3980 \text{ cm.}^{-1}$$

$$\delta(\pi) = 1450 \text{ cm.}^{-1}$$

The occurrence of CH_2 is without doubt as far as hydrocarbon chemistry is concerned as:

$$CH_2:CO + CH_2 \rightarrow C_2H_4 + CO \qquad (14)$$

(Olefin formation possible)

$$CH_4 \rightarrow CH_2 + H_2 \quad -47000 \text{ cal.}$$

$$E = 95 \text{ Kcal.} \qquad (15)$$

where E = activation energy,

if CH_2, then

$$CH_2 + CH_4 \rightarrow 2CH_3 \quad E = 12 \text{ Kcal.} \qquad (16)$$

$$CH_2 + CH_4 \rightarrow C_2H_6 + 36000 \text{ cal.},$$

$$E = 44 \text{ Kcal.} \qquad (17)$$

$$C_2H_4 \rightarrow 2CH_2 \quad -53000 \text{ cal.} \qquad (18)$$

$E = 77$ Kcal. (Kassel)[9]

$E = 150$ Kcal. (Rice)[10]

$$CH_2 + C_2H_4 = C_3H_6 \qquad (19)$$

$$CH_2 + H_2 = CH_4 + 47000 \text{ cal.}, \qquad (20)$$

$E = 32$ Kcal.[9]

$$CH_2 \rightarrow CH + H, \quad 90 \text{ Kcal. endothermic,}$$

$\overset{\circ}{\underset{\circ}{\circ}}$ extremely stable (21a)

$$2CH_2 \rightarrow C_2H_4 + 53000 \text{ cal.}, \qquad (21)$$

$E = 24$ Kcal.[9]

Voge[11] has calculated, from the Heitler-London-Pauling-Slater theory, the relative energies of formation of CH, CH_2, CH_3 and CH_4 as 4.0 e.v.

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(8) Mecke, Leipziger Vorträge, (1931), 46.
R. F. Barrow, T. G. Person and R. H. Purcell, *Trans. Faraday Soc.*, **35** (1939), 880.

(9) L. Kassel, *J. Am. Chem. Soc.*, **54** (1932), 3949.

(10) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals" (1935).

(11) (a) H. H. Voge, *J. Chem. Phys.*, **4** (1936), 581.
(b) G. Nordheim-Pöschl, *Ann. Physik*, **26** (1936), 258, 281 also gives estimates for the relative energies of CH_4, CH_3, CH_2 and CH based on the Heitler-London theory, and the results are in good agreement with those of H. H. Voge's calculation.

(92 Kcal.), 8.0 e.v. (184 Kcal.), 12.1 e.v. (279 Kcal.) and 17.0 e.v. (392 Kcal.) respectively. The value of 184 Kcal. for CH_2 is reasonable since it is practically twice the energy of C–H molecule (91 Kcal.) which is known from the spectroscopic data. The possibility that $CH_2+H_2 \rightarrow CH_4$ occurs at the surface of the vessel cannot be excluded at present; from the thermochemical evidence, the high reactivity with hydrogen is predictable. $CH_2+H_2 \rightarrow CH_4$ would be 80 Kcal.(*) exothermic whereas from Voge's data for CH_3 the alternative reaction, $CH_2+H_2 \rightarrow CH_3+H$, is 19 Kcal.(*) endothermic. The activation energy will be at least equal to the endothermicity and this is probably much greater than the activation energy of the highly exothermic reaction $CH_2+H_2 \rightarrow CH_4$ as pointed out by Bawn and Milsted;[11c] therefore $CH_2+H_2 \rightarrow CH_4$ is more probable, but as we already stated, during the normal synthesis, this reaction is found inhibited, i.e. CH_2(ad) interact much effectively with adjacent CH_2 (ad) as seen in Eqs. (20) and (21) through migration on the surface; concerning such possibility we will discuss a little later. Concerning the reaction (6)

$$\begin{array}{l} \quad\quad\quad\

$$\overset{\overset{OH}{|}}{C}\text{–H} + H_2 \rightarrow CH_2 + H_2O\,, \quad 48240 \text{ cal/mol} \qquad (29)$$

therefore at least the activation energy is 48240 cal./mol., so that if this type of reaction is proceeded through the molecules such as $\overset{\overset{OH}{|}}{C}\text{—H}$ $\underset{\underset{Co}{|}}{Co}\text{—}\underset{\underset{Co}{|}}{Co}\text{—Co}$ and H_2(ad) the reaction rate would be much accelerated to the extent of the heats of adsorption since

$$k' = z_0 e^{-\frac{E-Q_1-Q_2}{kT}} \qquad \text{i.e.}$$

the activation energy will be lowered by the amount of Q_1 and Q_2 where Q_1 is the heat of adsorption of $\overset{\overset{OH}{|}}{C}$—H on the catalyst surface and Q_2 is the heat of adsorption for H_2. Adopting the heat of adsorption for H_2 on Co practically the same as that of H_2 on Ni for which Beebe and Taylor[14] have given (12600–14600), 48240 cal/mol will be reduced by at least 13000 cal./mol. which means E is about 35000 cal./mol. Of course, further reduction will be possible by the heat of adsorption for HCHO on Co for which at present the value is not known.

The rôle played by CH_2 during the normal synthesis of the Fischer-Tropsch reaction are no longer doubtful as it is evidenced by various accumulated facts in hydrocarbon chemistry in general[15].

Starting from CH_2, if polymerized to C_2H_4, various reactions including polymerization and hydrogenation leading to higher hydrocarbons are quite easily attained as pointed out by Egloff, Schaad and Lowry[16], furthermore, Egloff and Wilson[17] pointed out that C_2H_4 acts as the key substance in hydrocarbon chemistry. Considering these, we have a very rational basis for our mechanism of the synthesis for which CH_2 plays the fundamental role in the formation of liquid hydrocarbons.

Egloff and Parrish[18] stated that the activation energies of the polymerization reaction of the olefins are about 38—40 Kcal. This is much less than the energy required to break the bonds, hence the polymerization predominates at lower temperature for all the olefins.

The activation energies of some of the polymerization reactions are shown in Table 4.

In connection with the polymerization of the adsorbed CH_2 molecules on the catalyst surface, we must conceive that these molecules migrate freely to interact with each other, i.e.,

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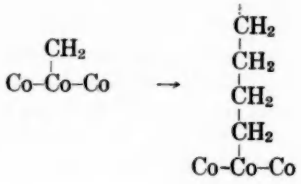
(14) Beebe and Taylor, *J. Am. Chem. Soc.*, **46** (1924), 43.
(15) (a) R. G. W. Norrish, *Proc. Roy. Soc.* (London) A, **150** (1925), 36.
(b) L. S. Kassel, *J. Am. Chem. Soc.*, **54** (1932), 3949.
(c) C. E. H. Bawn, *Trans. Faraday Soc.*, **34** (1938), 598.
(d) E. W. R. Steacie, *Chem. Rev.*, **22** (1938), 311.
(16) Egloff, Schaad and Lowry, *J. Phys. Chem.*, **35** (1931), 1825.
(17) Egloff and Wilson, *Ind. Eng. Chem.*, **27** (1935), 917.
(18) Egloff and Parrish, *Chem. Rev.*, **19** (1936), 145.

Table 4. The Polymerization of the Olefins.[19]

Reactions	E cal./mol.
$2CH_2 \rightarrow C_2H_4$	24000(*)
$2C_2H_4 \rightarrow C_4H_8$	37700 (**)
$2C_3H_6 \rightarrow C_6H_{12}$	37400
$2C_4H_8 \rightarrow C_8H_{16}$	38000
$2\text{-iso } C_4H_8 \rightarrow C_8H_{16}$	43000
$2C_5H_{10} \rightarrow C_{10}H_{20}$	38000



the above reaction is controlled by the freedom of migration. Fortunately, there are very good evidences that under certain condition, the adsorbed molecules are capable of moving laterally over the surface. These are principally connected with the metal atoms and molecules of organic compounds, of these compound movement, for various reasons migrations are easier to follow but we can draw by analogy certain conclusions as to the probable behavior of the adsorbed gas molecules. Volmer[20] has shown that when mercury atoms are condensed from the vapor on a suitably cooled surface, the crystals which form grow nearly 1000 times as fast as in some direction as in others. This can only be due to the migration of the condensed atoms over the surface of the growing crystal until they reach the position of the maximum stability. Estermann[21] has found the similar evidence in case of cadmium condensed from the vapor, and for crystal growth of benzophenone by Adhikari[22]. That Ba atoms can migrate in the same way over a tungsten surface has been demonstrated by Becker[23]. This fact is beautifully shown by measuring the variation of thermoionic emission. Adsorbed Caesium[24] has also been shown to migrate in the same way. Thus in the mechanism which the author proposed, the way of migration of CH_2 on the catalytic surface cannot be far from these definite evidences.

With regard to adsorption, we must remember that while adsorption is necessary for catalytic action, the maximum adsorption does not necessarily coincide with the maximum catalytic activity[25], as often erroneously stated by some investigators. The amount of adsorption increases with the decrease of temperature; the rate of adsorption and the rate of chemical reaction both decreases; there is, however, an optimum temperature depending on these factors. Taylor and Burns[25b] have definitely demonstrated that the maximum catalytic activity does not occur at the temperature at which the maximum adsorption in their experiment of

(*) Taken from L. Kassel (15b).
(**) $E = 38400$ and 38000, respectively, given in a later paper. (Krauze, Nemtzov and Soskina, *J. Gen. Chem.* (U.S.S.R.), **5** (1935), 382.
(19) Tabulated in: F. W. R. Steacie, *Chem. Rev.*, **22** (1938), 311.
(20) Volmer, *Trans. Faraday Soc.*, **28** (1932), 359.
(21) Estermann, *Z. Elektrochem.*, **31** (1925), 441; *Z. Physik*, **33** (1925), 320.
(22) Adhikari, *Z. Physik.*, **35** (1925) 170.
(23) Becker, *Trans. Faraday Soc.*, **28** (1932), 148.
(24) Taylor and Langmuir, *Phys. Rev.*, **44** (1933), 423.
(25) (a) Smithells, "Gases and Metals", (1938), p. 69.
(b) H. S. Taylor and R. M. Burns, *J. Am. Chem. Soc.*, **43** (1921), 1273.

hydrogenation of ethylene, and similar observations may be made with respect to a cobalt catalyst with carbon monoxide and hydrogen, and with nickel in the case of carbon dioxide and hydrogen. Considering these, again, we may say that Kodama's interpretation with regard to this phenomenon, i.e., the necessary coincidence of maximum catalytic activity and maximum adsorption is quite improbable (if there is, a happy coincidence). Of course, the magnitude of the heat of adsorption is definitely related to the catalytic activity by the relation already stated.

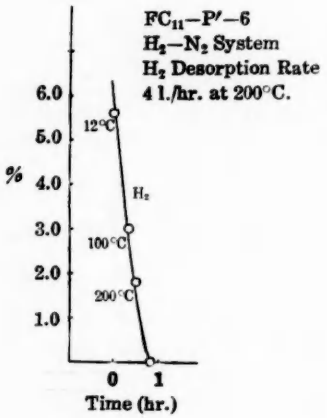


Fig. 5.

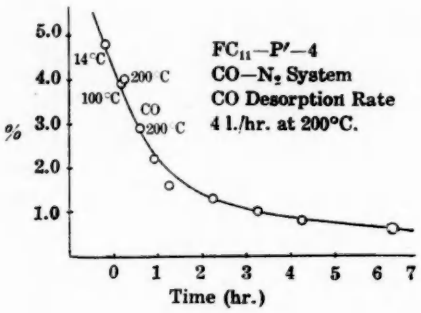


Fig. 6.

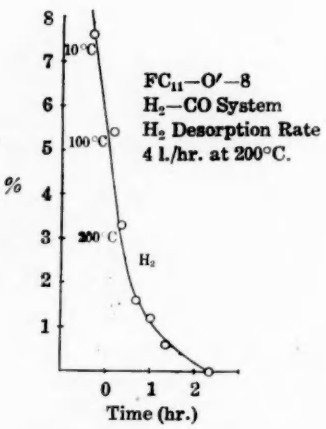


Fig. 7.

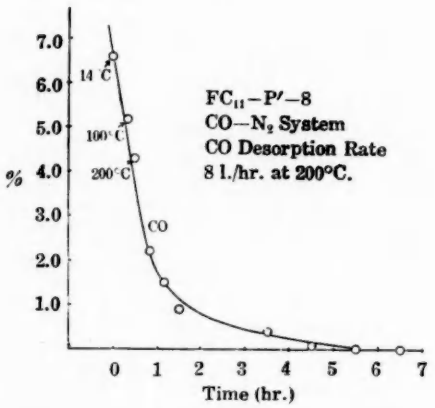


Fig. 8.

Furthermore, Taylor has demonstrated that carbon monoxide is very firmly adsorbed by metals and that at moderate partial pressure, it probably covers the metal surface completely. Thus, in such a case, H_2 in the

presence of CO can be adsorbed only on the surface of carbon monoxide and not on the metal surface.

With regard to this point that carbon monoxide is more firmly adsorbed on the surface of the catalyst has also been demonstrated in our desorption experiments of CO, H_2 and N_2 from the catalysts. The details of the experiments will be published in our subsequent paper. Figs. 5—8 show some of the adsorptive characteristics for H_2 and CO at 200°C.. The point that H_2 in the presence of CO can be adsorbed only on the surface of CO and not on the metal may be conceivable and furthermore, it is quite concordant with our mechanism, that is, in the Fischer–Tropsch reaction. When the catalyst at first is reduced by streaming H_2, such reduced catalyst is covered by adsorbed hydrogen. At the beginning, as a ($CO+2H_2$) mixture is passed, since CO is more strongly and easily adsorbed than H_2, it is quite reasonable to assume that some of the already adsorbed hydrogen is replaced by CO and some hydrogen remains, and the replaced hydrogen may immediately be attached to CO(ad), as shown in our mechanism, i.e., through the migration of the adsorbed molecule

$$\begin{array}{l} \mathrm{O} \\ \| \\ \mathrm{C} \\ | \\ \mathrm{Co\text{–}Co\text{–}Co} \end{array} + \mathrm{H_2(ad)} \rightarrow \begin{array}{l} \mathrm{OH} \\ | \\ \mathrm{C\text{–}H} \\ | \\ \mathrm{Co\text{–}Co\text{–}Co} \end{array}$$

This is quite reasonable from our approximate values of its activation energy which is 1000 cal./mol.(*); hence the above reaction is quite rapid. This value may correspond to the potential barrier for the process of surface migration[26].

J. K. Roberts[27] has also demonstrated that in his experiment of the adsorption of oxygen on a tungsten surface already covered with H_2, when an oxygen molecule is adsorbed, a hydrogen molecule is thrown off; every oxygen molecule adsorbed throws off a molecule of H_2. Moreover, he concluded that the hydrogen must be thrown off as molecule, not as separate atoms from his direct measurement of the heat of adsorption.

Considering the surface partially covered by oxygen, it is stated that the activated adsorption of hydrogen is connected with the interaction between hydrogen (thrown off hydrogen) and surface oxygen in the adsorbed state or that forming a integral part of the solid lattice.

This is quite analogous to our case of H_2 covered catalyst surface, once, it is partially replaced by CO and the fraction of H_2 is thrown off by CO, and immediately, through the surface migration, H_2 interacts with the adsorbed CO as shown in our theory.

Thus by applying our proposed mechanism to the Fischer-Tropsch reaction, all the facts of experimental observations are practically explained quite satisfactorily.

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(26) Lennard-Jones, *Trans. Faraday Soc.*, **28** (1932), 333. From the point of view of wave mechanics the question of surface migration has been considered by: Lennard-Jones and Strachan, *Proc. Roy. Soc.* (London), A **150** (1935), 442.

(27) J. K. Roberts, *Proc. Roy. Soc.* (London), A **152** (1935), 477.

(*) E. K. Rideal, *Trans. Faraday Soc.*, **28** (1932), 139, cites $E = 1000$ cal./mol. for the potential barrier for the process of surface migration in H_2 adsorbed on Ni from the experiment of Davisson and Germer, *Phys. Rev.* **2** (1927), 35, 705.

If the catalyst is of Fe type, our mechanism is equally satisfactory; the reactions (5) (6) (7) and (8) should proceed equally as well and in the presence of Fe catalyst, H_2O produced reacts as

$$CO + H_2O \rightleftarrows H_2 + CO_2 + 10.6\,\text{Kcal.} \qquad (30).$$

This reaction is quite fast over the Fe catalyst. The equilibrium is quite shifted to the CO_2 side as shown in the values of ΔF°.

Table 5.

Temp. °C.	ΔF° cal./mol.	
25°	−7241[28]	−6810[29]
100°	−6484	−6057
200°	−5494	−5115
300°	−4536	−4209
400°	−3611	−3340
500°	−2721	−2500

As observed experimentally, no H_2O formation but only CO_2, (of course, even in the case of Co and Ni type catalyst this water gas reaction is occurring) hence we observe a very slight amount of CO_2 formation as seen in the gas analysis data.

However, in the case of Fe catalyst usually the experiment is proceeded at above 250°C., and in such experimental conditions the reaction is quite rapid. If this is carried on at near 200°C., even in the Fe type catalyst, we have observed the formation of H_2O. This is quite obviously due to the fact that the H_2O formed during the synthesis is not used up rapidly enough in the water gas reaction to give CO_2, so that the CO_2 formation in the Fe catalyst is considered as secondary.

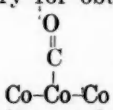
Table 6. Gas Analysis Data.

Types of catalyst	Co Type		Fe Type		(Co+Fe) Type	
Exp. No.	F_{45}—H	F_{45}—B(*)	F_{28}—A	F_{57}—C	F_{53}—D	F_{54}—C
CO_2	0.6	12.4	20.4	3.8	1.9	1.0
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.2
C_2H_4	0.4	0.3	0.8	0.2	0.2	0.0
CnH_{2n}	0.0	0.0	0.5	0.2	0.0	0.0
O_2	0.5	1.5	0.3	0.5	0.1	0.2
CO	30.5	1.6	26.2	45.2	33.1	30.0
H_2	63.9	30.1	50.3	46.6	60.0	65.5
CH_4	0.0	45.8	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0
N_2	4.1	8.3	1.5	3.5	4.7	3.1
Total	100.0	100.0	100.0	100.0	100.0	100.0

In the case of (Co+Fe) type catalyst, in which the experiment proceeded at 200°C., we demonstrated that the formation of H_2O is the same as in the case of Co catalyst.

(28) Lewis and Randall, "Thermodynamics", (1923) 575.
(29) J. Chipman, *Ind. Eng. Chem.*, **24** (1932), 1013.
(*) Initial stage of the reaction where CH_4 formation is predominating.

Thus we can safely say that our proposed mechanism explains very concordantly the experimental observations not only for Co and Ni type catalysts but also for Fe type catalyst for which, so far, it has been considered that an entirely different mechanism should play.

The inhibitive action of CO on the occlusive power of palladium for hydrogen was recognized by von Hemptinne.[30] This is similar to our results in that, when CO pretreatment at 350°C. was done for the catalyst, it destroyed the activity, i.e., when the CO treatment is made, the entire surface is covered by CO which may prevent the adsorption of H_2. This is necessary for obtaining the activated hydrogen which reacts with the adsorbed  to give CH_2 molecule (ad) for the regular synthesis of CH_2 (ad) → polymerization → desorption → hydrogenation → higher hydrocarbon. The Pd case seemed to be applicable also in the case of Co surface in the Fischer synthesis. This fact is very concordant with that when CO is used in the reduction of the catalyst at 350°C. instead of H_2 for the preparation of the catalyst, it does not show as good catalytic activity as when H_2 is used in the reduction. However, after the catalyst is being normally reduced by H_2 and then CO pretreatment was done at the temperature of reaction (190°–200°C.), then the activity is quite as good.

This is clearly shown in our experiment.

Table 7.

Various pretreatments for Co catalyst (XII_{16}–1)					
Subs.	Temp. °C.	React. Temp.	Activity	Exp. No.	Contraction (%)
CO	350°	200°	Activity destroyed. No oil formation.	FC_{11}–C	13
CO	200°	200°	Good.	FC_{11}–D	14
				FC_{11}–L	30
				FC_{11}–M	34
N_2	200°	200°	Not so good.	FC_{11}–J	28
				FC_{11}–H	31
H_2	200°	200°	Good.	FC_{11}–I	40
H_2	350°	200°	Not so good as at 200°C. with respect to its oil formation.	FC_{11}–F	21

The explanation for this is very clear as already discussed in connection with Roberts' experimental evidence and our desorption experiments.

The experimental data for the series of this investigation will be given in our subsequent papers to be published elsewhere.

(30) von Hemptinne, *Z. phys. Chem.*, **27** (1898), 429.

Summary.

(1) Introductory remarks for the Fischer-Tropsch reaction in connection with various mechanisms so far proposed are presented briefly.

(2) Our proposed mechanism is presented and discussed in detail.

(3) The role of CH_2 in hydrocarbon chemistry in general is stressed especially in connection with the Fischer-Tropsch reaction mechanism.

(4) Approximate values of the activation energies for the reactions involved in the synthesis are presented and discussed in correlation with adsorption.

(5) The aspect of polymerization process is discussed, and the question of surface migration is correlated with the polymerization reaction.

(6) Adsorption and catalytic activity involved in the synthesis are discussed in the light of our desorption experiment.

(7) The proposed mechanism is also applied to Fe type catalyst and discussed.

(8) Various pretreatment effects on the catalytic activity are discussed in the light of our experimental evidences.

In conclusion, the author expresses his hearty thanks to Dr. T. Marusawa, Former Director of the Institute, and Dr. S. Sato, Director of the Institute, for their interests and constant encouragement for carrying on this investigation and for the permission for this publication. Also the author takes this occasion to extend his thanks to Dr. R. Negishi who willingly has criticized and discussed the problem throughout this investigation—also to his colleagues; and to Messrs. S. Hayashi, Shimamura, Igarashi, Fujiwara and Kuwabara who were willing to assist in our experimental part of this investigation; and to Messrs. Kataoka, Inaba, Kodama and Nakano who have helped with their part in the analytic work.

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Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. III. Reduction Mechanism on the Ni-Thoria Catalyst.

By Kiyoshi MORIKAWA, Toraki KIMOTO, and Ryonosuke ABE.

(Received November 21, 1940.)

In the previous paper the cracking mechanism on the Pt-silica gel catalyst was elucidated. We are going to examine the reducing reactions which occur on the Ni-thoria catalyst. Experimental details are found in the previous papers.

I. Reduction on the Ni-Thoria Catalyst. The CO and CO_2 which are produced in the cracking zone at 950°C are reduced on the Ni-thoria catalyst in the hydrogen stream of about 5 l/hr.

$$CO + 3H_2 = CH_4 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$2CO + 2H_2 = CO_2 + CH_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2')$$

The high partial pressure of water vapour may prefer the reaction (2'), but in our analytical condition the situation is opposite and, therefore, this reaction may be duly discarded.

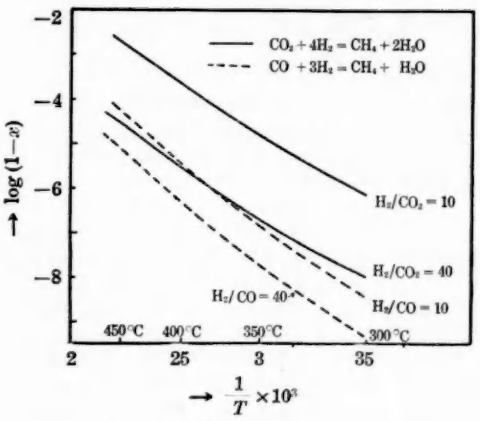

Fig. 12. Relation between Reaction Temperature and Rate of Reaction.

(1) *Reaction Temperature and Equilibrium Constants.* The equilibrium constants of reaction (1) and (2) decrease as the reaction temperatures are raised; therefore, the higher the reduction temperatures on Ni-thoria catalyst, the less favourable the equilibrium condition and the temperature of 350°C was found best suited for our purpose.

(2) *Calculation of Unreacted Carbon Oxides.* The relations between the reaction temperatures and unreacted carbon oxides are shown in Fig. 12 for the various ratios of H_2 to CO or CO_2.

In our analytical conditions the ratio of H_2 to CO may be around 7.2–12.8 and that of H_2 to CO_2 14.4–25.6 as already been discussed in the

previous paper. Fig. 12 definitely shows that above 400°C, even if the equilibrium state is nearly reached, the reduction of CO_2 may complete with difficulty.

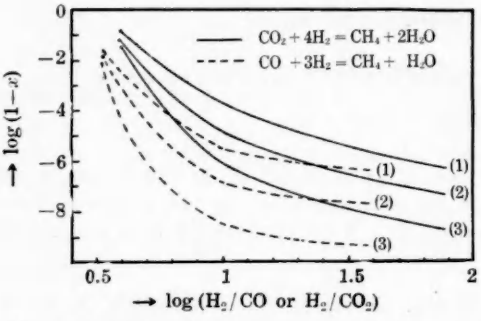

Fig. 13. Relation between reaction temperatures and ratio of concentration of reactants.

The relations between the logarithm of H_2/CO or H_2/CO_2 and the unreacted % of carbon oxides are plotted in Fig. 13.

Fig. 13 clearly shows that the decrease of hydrogen streaming velocity and consequently the decrease of hydrogen concentration or of H_2/CO and H_2/CO_2 inevitably increase the amount of unreduced carbon oxides. By the same reason the rapid cracking of sample results in the large partial pressures of carbon oxides and, therefore, brings the unsatisfactory results. The slow evaporation or decomposition of the sample is the key of success in this analysis.

(3) *Activity of Ni-Thoria Catalyst.* The Ni-catalyst was prepared after the method of H. S. Taylor and W. W. Russel[5] and contained 2% of thoria. The activity of this catalyst was examined by reducing CO_2 which was evolved from $NaHCO_3$. The production of CO_2 exactly followed the reaction,

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2 .$$

The results of table 9 proved that the activity of Ni-catalyst was quite satisfactory.

Table 9. Reducing activity of Ni-Catalyst.

Sample pure $NaHCO_3$, Hydrogen streaming velocity 4 l/hr.
Calculated: residue 63.19%, H_2O 10.72%, CO_2 26.19% (as H_2O, 21.45%) Total H_2O 32.17%

Exp. No.	Catalyst temp. °C	Sample gr.	Found				cal-Expt. ΔH_2O
			H_2O	CO_2 (as H_2O)		Residue.	
			%	%	%	%	%
C—61	295	0.1962	31.96	0	0	63.20	−0.21
C—60	315	0.2669	32.22	0.11	0.09	63.58	+0.05
C—58	350	0.2393	32.05	0	0	63.23	−0.12
C—59	350	0.2166	31.90	0.28	0.23	63.02	−0.27
C—62	400	0.2227	31.61	—	—	63.45	−0.56
C—63	400	0.3035	31.66	0.33	0.27	63.13	−0.51

(5) H. S. Taylor and W. W. Russel, *J. Phys. Chem.*, **29** (1925), 1325.

(4) *Hydrogenation Decomposition of Ethane and Ethylene.* The hydrocarbons higher than methane, i.e. ethane and ethylene, are easily and completely hydrogenated and decomposed to methane on the Ni-thoria catalyst[6] and, therefore, we are not concerned with the behaviour of these higher hydrocarbons which may be produced in the cracking reaction zone.

(5) *Effects of Water Vapour and Hydrogen Sulphide.* The oxidation of Ni-catalyst by the water vapour produced is impossible under the conditions employed.

$$Ni + H_2S = NiS + H_2$$

$$NiO + H_2S = NiS + H_2O$$

Poisoning effect of H_2S on Ni-catalyst is well known and, furthermore, water vapour produced in this reaction is the source of error in this analysis and, therefore, some device for the removal of H_2S prior to the reduction of carbon oxides is essential and will be discussed in the following paper.

II. Decomposition of Native High Molecular Compounds in the Hydrogen Stream. Saccharose, cellulose, lignin and brown coal of Jarahinohl mine (Manchoukuo) are decomposed at several temperatures in the hydrogen stream and the % of oxygen evolved as the volatile oxygen compound is measured by the method developed above. The variation of heating time of the sample between 10–30 minutes changed the % of oxygen found very little. Fig. 14 shows that the higher the polymerisation degree of the sample the more difficult it is to expel the oxygen from the sample and needs the higher temperature.

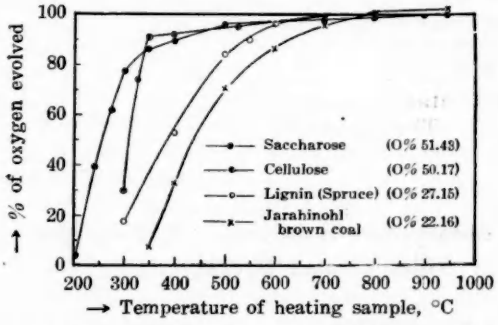

Fig. 14. Relation between the Temperature of Heating Sample and % of Oxygen Evolved from the High Molecular Compounds.

Table 10 is the classification of oxygen bonds in these samples and is compared with the results shown in Fig. 14.

It is well known that the initial decomposition of saccharose and cellulose is the liberation of water and, therefore, hydroxyl bond of alcoholic type is considered to be most unstable. Stabilities of pyran and furan rings or oxygen bonds of ether type placed between pyran and pyran or furan rings coming next; methoxyl bond and benzopyran or benzofuran ring seem to be most stable. Thus this analytical methods of oxygen in the organic compounds may be well employed for the study of thermal behaviour of high molecular compounds.

(6) Kiyoshi Morikawa, W. S. Benedict and H. S. Taylor, *J. Am. Chem. Soc.*, **58** (1936), 1795; Kiyoshi Morikawa, N. R. Trenner, and H. S. Taylor, *ibid.*, **59** (1937), 1103.

Table 10. Classification of Oxygen Bonds.

Sample	O found %	Classification of Oxygen bonds.					
		Alcoholic OH %	Pyran or furan %	Etheric* %	Methoxy %	Benzo-pyran or Benzo-furan %	Dimethylene Oxide %
Saccharose[7]	51.43	72.73	18.18	9.09	0	0	0
Cellulose[8]	50.17	60.00	20.00	20.00	0	0	0
Lignin[9] (spruce)	27.15	33.10	0	0	30.9	30.1	5.9
Brown coal (Jarahinohl)	22.16	—	—	—	—	—	—

* Oxygen bond placed between pyran and pyran or furan rings in cellulose or saccharose.

The authors wish to express their sincere thanks to Mr. Junichi Uchida, chief chemist of the Fiber Section of this Laboratory, who kindly gave much valuable informations on the native high molecular compounds.

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Thermal Diffusion of Binary Salt Solutions. A Note on the Paper of Gillespie and Breck.

By Kozo HIROTA.

(Received June 17, 1941.)

Introduction. In previous two papers (printed in Japanese), accepted by the Chemical Society of Japan on April 17 and May 27, the present author reported the method on the determination of thermal diffusion coefficient of solutions, using an apparatus of Clusius and Dickel,[1] and discussed the data thereby obtained and also reported preliminarily an "inverse" effect found in the binary solution of NaCl–HCl.

While these papers were being translated, a journal containing a paper of Gillespie and Breck, where the similar effect (in their $FeCl_3$–HCl

(7) Tollens-Elsner, "Kurzes Handbuch der Kohlenhydrate", 4 Ed., 477, (1935).
(8) W. N. Haworth and H. Machemer, *J. Chem. Soc.*, **1932**, 2270.
(9) K. Freuderberg, M. Meister, and E. Flickinger, *Ber.*, **70** (1937), 500; K. Freudenberg, F. Sohns and A. Janson, *Ann.*, **518** (1935), 62.

(1) K. Clusius and G. Dickel: *Naturwissenschaften*, **26** (1938), 546.

system) to that given in the author's second paper was described, came into his hand on the 3rd of June. For the purpose of comparing his result with theirs, his second paper is now translated with additional data for the HCl–NH_4Cl and a few remarks before the detailed experimental descriptions are published.

Experiments. The column consisted of two concentric boron glass tubes, having reservoirs of capacities 28 and 23 c.c. at the top and bottom ends, respectively. Width, length and volume of the annular space of the column were 1.5 mm. 94 cm. and 89 c.c., respectively. The higher temperature of the inner tube was maintained by the boiling point of carbon tetrachloride (76°C.) which was heated electrically, while the lower one of the outer tube by running water which was kept constant at 20°C. at the entrance and at 30°C. at the exit of the column, mean temperature difference thus being 51°C. The top reservoir was cooled as much as possible to protect the solution from evaporation and to circulate the solution freely.

At a fixed time after the experiment was begun, the content of each reservoirs was taken out, and the concentrations of the H^+ and Cl^- ions were analysed volumetrically, while those of the other ions were determined by the difference. The experimental results are summarised in Table 1 and 2, where every value is the mean of at least two measure-

Table 1.

Separation Ratio $\left(= \frac{\text{Concetration at the bottom reservoir}}{\text{Concentration at the top reservoir}} \right)$ of HCl–H_2SO_4.

Hours Elapsed	1			2			Infinite		
Ions	H^+	Cl^-	SO_4^{--}	H^+	Cl^-	SO_4^{--}	H^+	Cl^-	SO^{--}
1 N HCl	1.19_5	1.19_5	—	1.22	1.22	—	1.25	1.25	—
0.5 N HCl / 0.5 N H_2SO_4	1.19	1.21	1.18	1.23	1.23	1.22	—	—	—
1 N H_2SO_4	1.21	—	1.21	1.23	—	1.23	1.23	—	1.23

Table 2.

Separation Ratios of HCl–NaCl and HCl–NH_4Cl.

Hours Elapsed	1			2			Infinite		
Ions	H^+	Cl^-	Na^+ or NH_4^+	H^+	Cl^-	Na^+ or NH_4^+	H^+	Cl^-	Na^+ or NH_4^+
1 N NaCl	—	1.04_3	1.04_3	1 —	1.04_7	1.04_7	—	1.04_8	1.04_8
0.5 N HCl / 0.5 N NaCl	1.30_5	1.12	0.96	1.34	1.26	0.97	—	—	—
1 N HCl	1.19_5	1.19_5	—	1.22	1.22	—	1.25	1.25	—
0.5 N HCl / 0.5 N NH_4Cl	1.35	1.12	0.90	1.42	1.22	0.89	—	—	—
1 N NH_4Cl	—	1.00_8	1.00_8	—	1.01_0	1.01_0	—	1.01_0	1.01_0

ments, and those of the infinite hours were estimated by extrapolation, according to the theory of Debye. It was thus observed that in the system of HCl–H_2SO_4, the separation took place additively for the component salts, and that in the systems of HCl–NaCl and HCl–NH_4Cl, the concentration of H^+ ion became larger than that in system of HCl alone, while Na^+ and NH_4^+ ions were concentrated in the top reservoir. Such an "inverse" effect occurred especially more markedly in the HCl–NH_4Cl system.

Remarks. Because the annular space was constructed larger,*) in order to shorten the time of attainment of the stationary state, the observed effect was small when it was compared to that of Korsching and Wirtz[2] or to that of Gillespie and Breck, who used an apparatus with the annular space of 0.75 mm. and needed about one day for the attainment of the stationary state. But, as both the experimental conditions and the solutions were selected so as to be free from the ambiguity effected by creeping and hydrolysis of the solute, the "negative"[3] effect in the solutions, which contained H^+ and Cl^- ions, was confirmed without doubt.

In conclusion the author wishes to express his sincere thanks to Dr. R. Yoshimura, Director of the Department, for his interest and encouragement in carrying out this research.

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Analyse des Mineralwassers von Kinkei in der Provinz Totigi.

Von **Kazuo KURODA.**

(Eingegangen am 30. Juni 1941.)

Die Mineralquellen von Kinkei, in der Nähe des Berggipfels Keityo (Provinz Totigi), welcher ungefähr 1700 m. über dem Meeresspiegel liegt, wurden von T. Misawa vom therapeutischen Standpunkt aus genau untersucht. T. Misawa hat gefunden, dass das Trinken dieses Mineralwassers, wegen seines Kupferreichtums, Blutarmut heilt. Dieses Mineralwasser wurde im Jahre 1932 vom chemisch- hygienischem Laboratorium analysiert und im letzten Jahre von K. Kimura mit spektroskopischer Methode untersucht. Die Existenz folgender Elemente im Mineralwasser war mit spektroskopischer Methode gefunden (s. Tabelle 1).

(*) The details of the reason was described in the first paper which will be translated shortly.

(2) H. Korching and K. Wirtz: *Naturwissenschaften*, **27** (1939), 367.

(3) L. J. Gillespie and S. Breck: *J. Chem. Phys.*, **9** (1941), 370.

Tabelle 1. Resultat der spektroskopischen Analyse (K. Kimura).

Li(?)	Na	Cu	Ag(?)	Mg	Ca	Zn(?)	B(?)	Al	Si
Ti	Sn(?)	Pb	V	Bi	Cr	Mn	Fe	Co	Ni

Die Analyse geringer Quantität obengenannter Elemente im Mineralwasser ist sowohl therapeutisch wie auch geochemisch sehr interressant. Deshalb haben wir dieases Mineralwasser nach verschiedenen Methoden, d.h. spektroskopisch, polarographisch, colorimetrisch und gravimetrisch genau analysiert.

Das Kinkei-Wasser hat infolge seines hohen Ferrisulfatgehalts eine braun-gelbe Farbe. Durch Einwirkung der Luft setzen sich allmählich Niederschläge des Eisens ab. Thermometrische Beobachtungen und *p*H Messungen, welche am 5. Mai 1940 und am 2. Juni 1941 versucht worden, ergaben folgendes Resultat. (s. Tabelle 2).

Tabelle 2.

Datum	Temp. der Quelle °C.	*p*H-Wert
5. Mai 1940	10.0	2.4
2. Juni 1941	8.8	2.4

Das spezifische Gewicht des Mineralwassers verglichen mit destilliertem Wasser von 25°C. ist 1,003.

Kupfer, Blei, Kadmium, Nickel, Zink und Kobalt wurde durch Dithizon- Methode oder dithizon-polarographische Methode analysiert.(1) Vanadin, Chrom und Molybdän wurde nach der E. B. Sandellschen colorimetrischen Methode bestimmt.(2) Titan war nach der Wasserstoffperoxyd Methode,(3) Gallium und Beryllium war mit einer spektroskopischen Methode bestimmt.(4) Für die Bestimmung des Radons wurde ein I. M. Fontaktoskop von Dr. S. Iimori angewandt. Bei Ausführung der Analyse von übrigen Bestandteilen hielten wir uns an den gewöhnlichen Gang der Mineralwasseranalyse. Die vorgenommenen Bestimmungen ergaben die in nachfolgender Tabelle verzeichneten Resultate (s. Tabelle 3).

Wie man aus Tabelle 3 ersieht, ist der Hauptbestandteil dieses Mineralwassers Schwefelsäure, Eisensulfat, Aluminiumsulfat und Kieselsäure. Dieses Mineralwasser ist also eine vorbildlich saure Alaun-Vitriolquelle.

(1) Heller, Kuhla und Machek, *Mikrociehem* **23** (1937). 78.
Stout, Levy und Williams, *Collection Czechoslov. Chem. Commun.* **10** (1938), 129.
Kuroda, dies Bulletin, **15** (1940), 88, 439.
(2) Sandell, *Ind. Eng. Chem. Anal. Ed.*, **8** (1936), 336.
Kuroda, dies Bulletin, **14** (1936). 307.
(3) Snell, "Colorimetric Methods of Analysis", 1936 (New York) 355.
(4) Kuroda, dies Bulletin, **14** (1939), 305; *ibid.*, **15** (1940), 234 237.

Tabelle 3.

H^+	0.0033 g./l.	Zn	0.00011
K	0.000	Ti	0.0001
Na	0.001	Cr	0.000073
Ca	0.0150	Ni	0.000066
Mg	0.0032	V	0.000051
Fe^{++}	0.2836	Mo	0.000002
Fe^{+++}	0.2346	Ga	0.0000005 ~0.000001
Al	0.1067		
Cl	0.0180	Be	0.0000005 ~0.000001
SO_4^{--}	1.6397	Rn	0.00~0.05 (Mache)
HSO_4^-	0.3686	Pb	< 0.000010
H_2SiO_3	0.1339	Cd	< 0.000010
Cu	0.001033	Co	< 0.000010
As	0.0010		
Mn	0.00030		2.8658_{351}

Die Bestimmung des Abdampfrückstandes ergaben die in nachfolgender Tabelle verzeichneten Resultate (Tabelle 4).

Tabelle 4.

110 °C.	3.62 g./l.
140 °C.	3.49
> 1 00°C.	1.125

Dieses Mineralwasser wurde im Jahre 1932 zweimal vom chemisch-hygienischem Laboratorium analysiert. In Tabelle 5 haben wir unser Analysenresultat mit dem Resultat des chemisch-hygienischen Laboratoriums verglichen.

Tabelle 5 zeigt eine bedeutende Zunahme des Eisens; Aluminium und Kieselsäure hatten jedoch etwas abgenommen. Das Sulphat hat sich ungeheuer vermehrt, im gegensatz dazu hat sich die freie Schwefelsäure fast nicht verändert.

Tabelle 5.

	Chemisch-hygienischer Laboratorium zu Tokyo		Kuroda
	Mai 1932	Oktober 1932	Juni 1941
H^+	0.0033	0.004507	0.0038
K	0.0023	0.002056	0.000
Na	0.0117	0.0152	0.001
Ca	0.0035	0.002997	0.0150
Mg	0.0026	0.002793	0.0032
Fe^{++}	0.0043	0.0312	0.2836
Fe^{+++}	0.1643	0.1457	0.2346
Al	0.1324	0.1444	0.1067
Cu	—	0.0006	—

Tabelle 5. (*Fortsetzung*)

	Chemisch-hygienischer Laboratorium zu Tokyo		Kuroda
	Mai 1932	Oktober 1932	Juni 1941
Cl	0.0190	0.002965	0.0180
HSO_4^-	0.3169	0.4375	0.3686
SO_4^{--}	1.1599	1.245	1.6897
HBO_2	0.1153	—	—
H_2SiO_3	—	0.1562	0.1389
	1.9371	2.191	2.8641
Spezifische Gewicht	1.0004	1.001	1.003
*p*H-Wert	2.39	2.26	2.4

Ich möchte hiermit Herrn Prof. Kenjiro Kimura für seine freundliche Anleitung und steten Ratschläge, die mir bei der Ausführung dieser Arbeit zuteil gewordn sind, meinen herzlichsten Dank aussprechen. Herrn Prof. Yuji Shibata möchte ich für sein warmes Interesse an dieser Arbeit ergebenst danken. Der Kaiserlichen Akademie der Wissenschaft sowie der Notgemeinschaft der japanischen Wissenschaft sind wir wegen ihrer finanziellen Unterstützung zu grossem Dank verpflichtet.

Chemisches Institut,
Naturwissenschaftliche Fakultät,
Kaiserliche Universität zu Tokyo.